MODELING FOR METALS CONTAMINATED WASTEWATER BY ALGAE ADSORPTION

PORNWILAI CHANKITKAN

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Student	Pornwilai Chankitkan
Student ID	52650751
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ABSTRACT

We studied the ability of algae adsorption in wastewater polluted by alloys. A mathematical model is developed to describe the biosorption of metals by algae in the contaminated water. The numerical, steady state and analytic solutions are obtained by using Crank – Nicolson method and by using similarity method. The results provides understanding the advection and diffusion of metals in the contaminated water at various times and positions. It was found that the concentration of metals in the contaminated water consisting of the algae decreases over time and asymptotically reaches the equilibrium state. Moreover, the analytic results were validated by comparing with experimental data. This work is expected to greatly benefit an environmental science particularly concerning the wastewater treatment.

Keywords: Biosorption, Wastewater, Advection, Diffusion, Crank – Nicolson Method, Steady State, Similarity Method, Equilibrium State

หัวข้อวิทยานิพนธ์	แบบจำลองการดูดซับปริมาณโลหะที่ปนเปื้อนในน้ำเสียโดยใช้สาหร่าย
นักศึกษา	นางสาวพรวิลัย ชาญกิจกรรณ์
รหัสประจำตัว	52650751
ปริญญา	วิทยาศาสตรมหาบัณฑิต
สาขาวิชา	คณิตศาสตร์ประยุกต์
พ.ศ.	2556
อาจารย์ที่ปรึกษา	ดร.บุษยมาส พิมพ์พรรณชาติ

บทคัดย่อ

งานวิจัยนี้ศึกษาการดูดซับปริมาณโลหะที่ปนเปื้อนในน้ำเสียโดยใช้สาหร่ายดูดซับ โดยงานวิจัยได้พัฒนาแบบจำลองทางคณิตศาสตร์ของสมการการแพร่-พาโดยมีการเพิ่มเทอมของสมการการดูดซับเข้าไปและได้ทำการหาผลเฉลยเชิงตัวเลขโดยวิธีแครงก์ นิโคลสัน(Crank – Nicolson method) หาผลเฉลยที่สภาวะสมดุลของแบบจำลอง (Steady State Solution) และหาผลเฉลยแม่นตรงโดยวิธีทางคณิตศาสตร์ที่เรียกว่าซิมิลาร์ริตี้เมทตอด (Similarity Method) เพื่ออธิบายปริมาณโลหะปนเปื้อนที่เหลืออยู่ในน้ำเสีย ณ เวลาและตำแหน่งต่างๆหลังจากที่สาหร่ายได้ทำการดูดซับไปแล้ว ซึ่งจากผลเฉลยเชิงตัวเลขและผลเฉลยแม่นตรงของแบบจำลองทำให้ทราบว่าปริมาณโลหะปนเปื้อนในน้ำเสียมีค่าลดลงจนเข้าสู่สภาวะสมดุลอันเนื่องมาจากการดูดซับของสาหร่าย นอกจากนี้ผลเฉลยที่ได้จากสมการที่เราพัฒนาขึ้นมาใหม่ยังสอดคล้องกับผลการทดลองในงานวิจัย

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Introduction

1. Background and Rationale

Nowadays wastewater is one of the major problems of environment stemming from community, agriculture and industrial effluents which are different amount of the byproduct of industrialization. With the increase in industrial nowadays, the problem of wastewater has become even more severe especially with lacking of good wastewater management. Industrial wastewaters differ in their impurities and here metals contaminated wastewater is considered for treatment aspect using microalgae. Normally, wastewater treatment can be as simple as chemical addition or as complex as the combination of multiple unit processes for a complete water treatment system. Here the process of adsorption is focused. The microalgae is used as an adsorption agent, thus the process is so called biosorption. Because aerobic treatment reservoir in our system has abundant the algae and aquatic plant, they then act as wastewater cleaning metal alloys agent in the contaminated water. The mathematical model is developed to describe the biosorption of metals by algae in the contaminated water and the analytic solution is obtained for having insight into the problem

2. Purpose of the Study

1. To analyze the concentration of metals remaining in the contaminated wastewater after adsorbed by algae.
2. To use numerical method for computing approximate solutions of mathematical model.
3. To use similarity method for finding analytical solution of mathematical model.
4. To create a Matlab code for showing the behavior of the concentration of metals remaining in the contaminated wastewater at any time and various distances.

3. Scope of the Study

We will study concentrations of metals in the remaining of the contaminated wastewater at various distances after adsorbed by algae. Moreover, we also find numerical solution by Crank Nicolson method and analytical solution by Similarity method. And we compare experimental data of the adsorption of malachite green onto *Phithophora sp.* [4]. and adsorption of chromium (VI) from electroplating factory by chitosan resin [9]. with analytical solution.

4. Method

1. Studing the adsorption process by algae of metals in contaminated wastewater.
2. Developing mathematical model to explain and analyze concentrations of metals remaining in the contaminated wastewater.
3. Studying the adsorption by algae.
4. Solving numerical and analytical solutions at any time and various distances.
5. Comparing analytical solution with experimental data.

5. Utilization of the Study

1. Understanding about processing adsorbed of metals in the contaminated wastewater by biomass.
2. Understanding about adsorption of mathematical model.
3. For analytical solutions of concentration remaining in the contaminated wastewater after adsorbed by algae at various distances.
4. Be able to use mathematical model for computing concentration of metals in the contaminated wastewater at any time and various distances.

Chapter 2

Theory and Literature Reviews

This research we study about adsorption of metals in the contaminated wastewater by algae. In this chapter we describe about wastewater treatment, adsorption, equation of adsorption and methods for solving mathematical model.

2.1 Wastewater Treatment

The purpose of wastewater treatment is to remove the contaminants from water so that the treated water can meet the acceptable quality standards. The quality standards usually depend upon whether water will be reused or discharged into a receiving stream. Available wastewater treatment processes can be broadly classified as physical, chemical or biological. These processes, which consisting of a series of unit operations, are applied in different combinations and sequences depending upon the prevailing situations of influent concentration, composition and condition and specifications of the effluent.

Physical processes are based on exploitation of the physical properties of the contaminants and are generally the simplest forms of treatment. These principally comprise screening, sedimentation, flotation and filtration. Chemical processes utilize the chemical properties of the impurities or of the added reagents. Commonly used chemical processes are precipitation, coagulation, and disinfection. Other physical and chemical processes such as air stripping, carbon adsorption, oxidation and reduction, ion exchange and membrane processes like reverse osmosis and electrodialysis are also important in certain particular cases. Biological processes utilize biochemical reactions; typical examples are biological filtration and the activated sludge process.

The wastewater treatment processes are generally grouped according to the water quality they are expected to produce. These processes are usually grouped as the primary treatment, the secondary treatment, and the tertiary or the advanced waste treatment. Primary treatment removes identifiable suspended solids and floating matter. In the secondary treatment, also known as the biological treatment, organic matter that is soluble or in the colloidal form is removed. Advanced waste treatment may involve physical, chemical or biological processes or their various combinations depending on the impurities to be removed. These processes are employed to remove residual soluble non – biodegradable organic compounds, including surfactants, inorganic nutrients and salts, trace concentrations of various types, and dissolved inorganic salts. The advanced waste treatment processes are expensive, and are used only when water produced is required to be of higher quality than that produced by conventional secondary treatment so that the treated water can be reclaimed and put to some form of direct re – use.

2.2 Biological Treatment

Biological treatment has been very successful in the removal of organic pollutants and colloidal organics from wastewater. Activated sludge, biological filters, aerated lagoons, oxidation ponds, and aerobic fermentation are some of methods available for wastewater biodegradation. In the removal of toxic waste, more care is needed since the bacteria can be destroyed from shock loading or increases of toxic material fed in without allowing time for the population to grow large enough to deal with it.

Biodegradation occurs because bacteria are able to metabolize the organic matter through enzyme systems to yield carbon dioxide, water, and energy. The energy is used for synthesis, motility, and respiration. Simple dissolved matter is taken into the cell and oxidized, but with more complex inorganics, enzymes are secreted extracellularly to hydrolyze the proteins and fats into a soluble form which can then be taken into the cell and oxidized. Hence, more complex matter takes longer to process. Some organic compounds are "refractory," they cannot be oxidized while others are toxic to the bacteria at high concentrations.

The purpose of biodegradation is to convert the waste into end – products and material that will settle and can be removed as sediment. Again, biodegradation may not be 100%. Also, toxic byproducts may be formed. Further treatment by chemical methods or dilution may be needed to get the contaminant to a concentration prescribed as safe.

Nitrogen (N) and phosphorous (P) are essential in the oxidation process for the synthesis of new cells. Trace amounts of potassium and calcium are also required. The former are sometimes deficient, so nitrogen is added in the form of ammoniacal nitrogen (nitrite and nitrate are not readily used by bacteria).

BOD, or Biochemical Oxygen Demand, measures the strength of the organics present and is defined as the amount of oxygen needed by the bacteria for oxidation. The more concentrated the organic material, the higher the BOD. A BOD: N: P ratio of 100:5:1 is thought to be the optimum ratio of nutrients needed by bacteria.

In this research we focus on a type of wastewater treatment pond which stabilization ponds. The specification is shown the following next subtopic.

2.1.1 Stabilization Ponds

In this process, wastewater is stabilized by the actions of bacteria in shallow ponds. There are basically two types of ponds: one where there is a natural supply of oxygen from algae photosynthesis (oxidation ponds), and mechanically – supplied – oxygen ponds. The bacteria metabolize the wastes and the solids settle at the bottom as sludge. Also, there is anaerobic decomposition, with an interchange of products between the two layers of bacteria in a symbiotic relation.

Due to oxidation ponds has been widely used as a collective term for all types of ponds. Originally, an oxidation pond was a pond that received partially treated wastewater. Type of oxidation ponds are Aerobic ponds, Facultative ponds, Anaerobic ponds, Maturation ponds and Aerated lagoons. In this research we are interest wastewater treatment by algae, and then next subtopic is described of aerobic ponds.

2.1.2 Aerobic Ponds

The aerobic pond is a shallow pond less than 1 m in depth. Which light penetrates to the bottoms, thereby maintaining active algae photosynthesis throughout the entire system. During the daylight hours, large amounts of oxygen are supplied by the photosynthesis process; during the hours of darkness, wind mixing of the shallow water mass generally provides a high degree of surface reiteration. Stabilization of the organic material entering an aerobic pond is accomplished mainly through the action of aerobic bacteria.

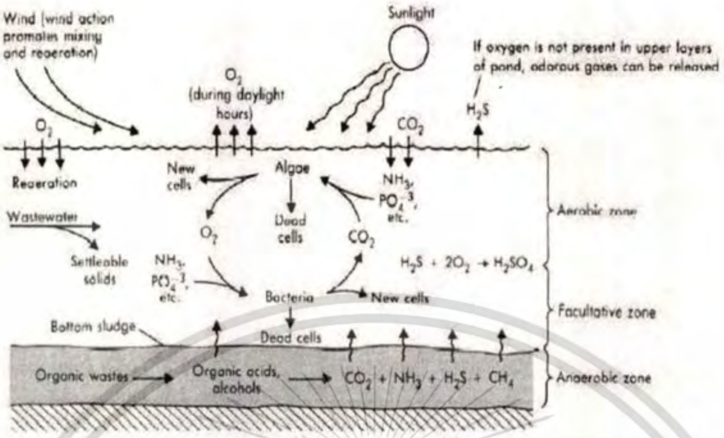

Fig.2.1 Operation of the facultative ponds system (Tchobanoglous and Schroeder 1987)

Biological pond systems are traditionally designed on the basis of average liquid detention time and organic loading per unit surface area, or both. Typical design parameters are summarized in Table 2.1. The advantages of the biological pond system are their simplicity of operation and low costs.

Table 2.1 Empirical pond design parameters

Pond type	**Depth (m)**	**Loading (kg BOD/m^2.Day)**	**Detention time (days)**	**% BOD removal**
Aerobic	0.5 – 1.0	0.15	2 – 6	80 - 95
Facultative	1.0 – 2.0	0.05	5 – 30	70 - 85
Aerated	2.0 – 4.0	0.2	2 – 10	50 - 90
Anaerobic	2.5 – 5.0	0.5	30 – 60	50 - 70

2.3 Sorption

Sorption is a process whereby a dissolved substance is transferred to and becomes associated with solid material. It includes both the accumulation of dissolved substances on the surface of solids (***adsorption***) and the interpenetration or intermingling of substances with solids (***absorption***). The substance that is sorbed is called the ***sorbate*** and the solid is called the ***sorbent***. ***Desorption*** is the process whereby a sorbed substance is released from a particle.

For neutral organics, several mechanisms underlie the sorption process. These included (Schwarzenbach et al. 1993):

1. Hydrophic effects cause the sorbate to associate with organic matter in the particular phase because of an unfavorable free – energy cost of staying in solution.
2. Weak surface interactions via van der Waals, dipole – dipole, induced dipole, and other weak intermolecular forces.
3. Surface reactions where the sorbate actually bonds to the solid.

For charged toxins, the additional mechanism of ion exchange can occur. It should also be mentioned that, aside from organically rich materials, neutral organic chemicals are also sorbed by solids with little or no organic content. For such cases the sorbent consists of inorganic matter such as clays. Such inorganic solid sorption is usually significant only when the organic carbon content of the solids is quite low.

2.3.1 Adsorption

Adsorption processes have been used since the 1950s for the high-efficiency removal of a wide variety of organic vapors and several types of inorganic gases. The use of adsorption processes has been expanding recently due to innovations in the designs of the systems and to the development of new adsorbents.

Adsorption systems designed for odor control and other low contaminant concentration applications (<10 ppm) are relatively simple. In these cases, the adsorbent bed is discarded as it approaches saturation with the contaminant.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial application such as activated charcoal, synthetic resins and water purification.

2.3.2 Adsorption Forces

The adsorption process is classified as either physical or chemical. The basic difference is the strength in which the gas molecule is bonded to the adsorbent. In physical adsorption, the gas molecule is held to the solid surface by weak forces of intermolecular cohesion. The chemical nature of the adsorbed gas remains unchanged; therefore, physical adsorption is a readily reversible process. In chemical adsorption a strong chemical bond is formed between the gas molecule and adsorbent. Chemical adsorption, or chemisorptions, is not easily reversed.

Physical Adsorption

The forces active in physical adsorption are electrostatic in nature and occur under suitable conditions in most gas-solid systems. These forces are present in all states of matter: gas, liquid, and solid. They are the same forces of attraction that cause gases to condense and deviate from ideal behavior under extreme conditions. Physical adsorption is also referred to as van der Waals' adsorption. Because of Van der Waals' forces, physical adsorption can form multiple layers of adsorbate molecules, one on top of another.

The electrostatic effect that produces Van der Waals' forces depends on the polarity of both the gas and solid molecules. Molecules in any state are either polar or nonpolar depending on their chemical structure. Polar substances exhibit a separation of positive and negative charges within the compound, which is referred to as a permanent dipole. Water is a prime example of a polar substance. Nonpolar substances have both their positive and negative charges in one center so they have no permanent dipole. Most organic compounds are nonpolar because of their symmetry.

Chemical adsorption

Chemical adsorption (chemisorption) results from a chemical interaction between the gas and the solid. The gas is held to the surface of the adsorbate by the formation of a chemical bond. Adsorbents used in chemisorption can be either pure substances or chemicals deposited on an inert carrier material. One example of the former is the use of pure iron oxide chips to adsorb hydrogen sulfide gas. An example of the latter is the use of activated carbon that has been impregnated with potassium iodide to remove mercury vapors. All adsorption processes are exothermic whether adsorption occurs from chemical or physical forces. The fast-moving gas molecules lose kinetic energy when adsorbed on the solid, which results in the liberation of heat.

2.4 Adsorption Kinetics

Kinetics study is an important part of researches in adsorption area because the mechanism of the process can be realized by kinetic constants. Knowledge about kinetic parameters provides valuable insight into the reaction pathway. As well the rate of adsorption which controls the resistance time is determined by kinetics.

2.4.1 Pseudo First Order Kinetic Model

The pseudo – first – order rate expression of Lagergren is a widely used kinetic model for adsorption data analysis. This kinetic model is used for reversible reaction with an equilibrium being established between liquid and solid phases it is represented by equation (2.1),

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (2.1)$$

Integrating equation (2.1) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, results to the following equation (2.2),

$$\ln\frac{(q_e - q_t)}{q_e} = -k_1 t \qquad (2.2)$$

Which may be rearranged to form,

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (2.3)$$

Where q_t is the sorbent uptake capacity (mg/g^{-1}) at any time t, q_e denotes the sorbent uptake capacity (mg/g^{-1}) at equilibrium and k_1 (min^{-1}) is the observed rate constant of pseudo – first – order kinetics model.

2.5 Ability of Adsorption of Biomass

Biomass is any organic matter - wood, crops, seaweed, animal wastes that can be used as an energy source. Biomass gets its energy from the sun. During a process called photosynthesis. This my research studies about adsorption by biomass. Then algae biomass used in this research. In next table shows type of algae biomass for metal adsorption in the contaminated wastewater.

Table 2.2 Ability of adsorption of species of algae, fungus, yeast and bacteria.

Biomass	Amount of adsorption metals contaminated
Algae	
Chlorella emersonii	Cadmium
Sargassum muticum	Cadmium
Ascophylluum sargassum	Lead, Cadmium
Ulva reticulate	Copper (Cu(II))
Brown sea weeds	Cromium
Ecklonia species	Copper (Cu(II))
Fungus	
Phanerochaete chrysosporium	Nickel (Ni (II)), Lead (Pb (II))
Aspergillus niger	Cadmium
Aspergillus fumigatus	Erronium (Ur (VI))
Aspergillus terreus	Copper
Penicillium chysogenum	Gold
Yeast	
Saccharomyces cerevisiae	Uranium, Cadmium, Mercury
Kluyveromyces fragillis	Mercury (Hg (II)), Cadmium
Bacteria	
Bacillus polymyxa	Copper
Bacillus coagulens	Chromium (Cr (VI))
Eschereria coil	Mercury, Copper, Chromium, Nickel
Pseudomonas species	Chromium (Cr (VI)), Copper(Cu (II)) Cadmium (Cd(II)), Nickel (Ni (II))

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2.6 Numerical Solution of Partial Differential Equations Using Finite Difference Method

2.6.1 Crank – Nicolson Implicit Method

Although the explicit method is computationally simple it has one serious drawback. The time step $\delta t = k$ is necessarily very small because the process is valid only for $0 < k / h^2 \leq \frac{1}{2}$, and $h = \delta x$ must be kept small in order to attain reasonable accuracy. Crank and Nicolson (1974) proposed, and used, a method that reduce the total volume of calculation and is valid for all finite values of r whereas $r = k / h^2$. They replaced $\partial^2 u / \partial x^2$ by the mean of its finite – difference representations on the $(j+1)$th and jth time rows and approximated the equation. [8]

$$\frac{\partial U}{\partial t} \simeq \frac{\partial^2 U}{\partial x^2} \tag{2.4}$$

whereas

$$\frac{\partial U}{\partial t} \simeq \frac{U_{i,j+1} - U_{i,j}}{k} \tag{2.5}$$

$$\frac{\partial^2 U}{\partial x^2} \simeq \frac{1}{2}\left(\frac{U_{i+1,j+1} - 2U_{i,j+1} + U_{i-1,j+1}}{h^2} + \frac{U_{i+1,j} - 2U_{i,j} + U_{i-1},j}{h^2}\right) \tag{2.6}$$

Consider equation 2.3, hence;

$$\frac{U_{i,j+1} - U_{i,j}}{k} = \frac{1}{2}\left(\frac{U_{i+1,j+1} - 2U_{i,j+1} + U_{i-1,j+1}}{h^2} + \frac{U_{i+1,j} - 2U_{i,j} + U_{i-1,j}}{h^2}\right) \tag{2.7}$$

In general, the right hand side of (2.7) contains three unknowns i.e., ($U_{i-1,j+1}$, $U_{i,j+1}$ and $U_{i+1,j+1}$) and ($U_{i-1,j}$, $U_{i,j}$ and $U_{i+1,j}$ in the left side), pivotal values of U (Fig. 2.2)

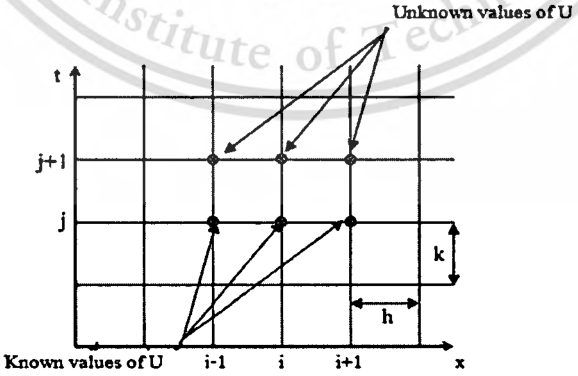

Fig. 2.2 Mesh point of Crank – Nicolson Method

2.8 Literature Reviews

In (2005), Kumar and co-workers [5]. studied about adsorption of malachite green onto *Phithophora sp.* with the initial malachite green of 20-100 mg/l. They found that algae posses some capacity to uptake 64.4 mg/g at higher dye concentration of 100 mg/l and approach the equilibrium state around at 50 minutes. Recently, Sukhuum and Inthorn [6] .have studied about removal of Cr^{+3} by *Rivularia sp.* and *Stigonema minutum.* They considered the initial concentration of Cr^{+3} 500 mg/l and found that *Rivularia sp.* and *Stigonema minutum* had the highest Cr^{+3} adsorption at 38.27 and 43.59 mg/g then reached equilibrium state at 120 minutes.

In this study the ability of algae adsorption in wastewater polluted by alloys was investigated and mathematically analyzed particularly on concentration of metals in contaminated water by using mathematical model at any time and various distances.

Chapter 3

Methodology for Analysis of the Model

In chapter 3 we develop adsorption equation by using pseudo first order kinetic model for our model. After that we find numerical solution by Crank – Nicolson implicit method and solve analytic solution by Similarity method for explaining concentrations of metals remaining in the contaminated wastewater at any time and various distances.

3.1 Model Formalism

We begin with mass balance law stating that the remaining concentration of metals in the contaminated water is

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} + f(t) \qquad (2.8)$$

where C is the remaining concentration of metals in the contaminated water (mg/l), D_x is a diffusion coefficient (m^2/hr), v is the velocity in the x direction (m/hr), t is time of adsorption (hr), x is a distance (m), $D_x\left(\partial^2 C/\partial x^2\right)$ is diffusion term depend on the flow character in the ponds, $v(\partial C/\partial x)$ is convection term and function $f(t)$ is adsorption term.

Our next goal is to find the explicit form of the function $f(t)$. We begin with pseudo first order kinetic model:

$$\int_{q_0}^{q_t} \frac{dq}{(q_e - q)} = \int_0^t k_1 dt$$

$$\ln(q_e - q_t) - \ln(q_e - q_0) = -k_1 t$$

$$\ln\frac{(q_e - q_t)}{(q_e - q_0)} = -k_1 t$$

$$\frac{(q_e - q_t)}{(q_e - q_0)} = e^{-k_1 t}$$

$$q_e - q_t = e^{-k_1 t}(q_e - q_0)$$

$$q_t = q_e - e^{-k_1 t}(q_e - q_0)$$

Therefore we have, $q_t = q_e + e^{-k_1 t}(q_0 - q_e)$ (2.9)

where q_0 is the initial amount of adsorbate per unit mass of algae (mg/g), q_e and q_t are the amounts of adsorbate per unit mass of algae at equilibrium state and any time (mg/g), respectively, and k_1 is constant rate of first order biosorption (1/hr). Next, we transform unit of the amount of adsorbate per unit mass of algae (mg/g) to unit of the mass of adsorbed metals on algae (mg).

Thus we use the amount of adsorbate per unit mass of algae is the mass of adsorbate of algae divided by the mass of algae, we have

$$q_0 = \frac{M_{0al}}{M_s}, \quad q_t = \frac{M_t}{M_s}, \quad q_e = \frac{M_{al}}{M_s} \tag{3.0}$$

where M_s is the mass of algae (mg), M_{0al}, M_t and M_{al} is the mass of adsorbed metals on algae at initial time, any time and equilibrium state (mg), respectively.

Substituting (3.0) into (2.9), we obtain,

$$M_s.q_t = M_s.q_e + e^{-k_1 t}(M_s.q_0 - M_s.q_e)$$

$$M_t = M_{al} + e^{-k_1 t}(M_{0al} - M_{al}) \tag{3.1}$$

In our model analyze the remaining concentration of metals in the contaminated water. Thus we employ the conservation of mass stating that the remaining mass of metals after adsorbed by algae in the contaminated water is the difference between the initial mass of the alloys in the wastewater and the adsorbed mass on algae.

$$M = M_0 - M_t \tag{3.2}$$

where M is the mass of metals remaining in the contaminated water (mg), M_0 is the initial mass of metals in the contaminated water (mg), and M_t is the adsorbed mass on algae at any time (mg). From conservation of mass we substitute (3.1) into (3.2), we obtain

$$M = M_0 - M_{al} + e^{-k_1 t}(M_{0al} - M_{al}) \tag{3.3}$$

The remaining concentration of metals in the contaminated water is obtained by dividing (3.3) by a constant volume V:

$$C = C_0 - (C_{al} + e^{-k_1 t}(C_{0al} - C_{al}))$$

where C_0 is the concentration of metals adsorbed on the algae at initial time, C_{al} is the concentration of metals adsorbed on the algae at equilibrium state and C_{0al} is the concentration of metals adsorbed on the algae at initial time (we decide C_{0al} equal zero because the concentration of adsorbed metals on the algae at initial time without metal adsorbate). Then we simplify to above equation in the form,

$$C = e^{-k_1 t}C_{al} + (C_0 - C_{al}). \tag{3.4}$$

Differentiating (3.4) with respect to t. The equation (3.4) can be rewritten as:

$$\frac{dC}{dt} = -k_1 C_{al} e^{-k_1 t}$$

The function $f(t)$ is adsorption term. Then we let differential equation can be replaced by function $f(t)$. From above equation simplify to autonomous system we have:

$$f(t) = -k_1\big(C - (C_0 - C_{al})\big) \tag{3.5}$$

Substituting (3.5) into (2.8) yields:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - k_1(C - (C_0 - C_{al})) \tag{3.6}$$

The initial condition is $C(x,0) = C_0,\ 0 \le x \le L$ and the boundary conditions are

$C(0,t) = A_1,\ t > 0$ and $\dfrac{\partial C(L,t)}{\partial x^{*}} = 0,$ for all x and t.

The equation (3.6) is our model for solving by numerical and analysis solutions in the next section.

3.2 Mathematical Model and Dimensionless Variable

Previous to, the equation (3.6) will be solved numerical solution by Crank – Nicolson implicit method. We have to simplify (3.6) of dimensionless parameter and variable whereas for all independent and dependent variables on interval $[0,1]$. Therefore we define new independent and dependent variables in form,

$$U=\frac{C}{C_N},\quad \tau=\frac{t}{T},\quad \xi=\frac{x}{L} \tag{3.7}$$

Let $C\in[0,C_N]$, $t\in[0,T]$ and $x\in[0,L]$ whereas L is the length of ponds, T is time. And when C_N is the remaining concentration of metals in the contaminated water.

Thus, $$C=UC_N\ ,\quad t=\tau T\ ,\quad x=\xi L$$

Therefore, $$\frac{\partial C}{\partial t}=\frac{C_N}{T}\frac{\partial U}{\partial \tau}\ ,\quad \frac{\partial C}{\partial x}=\frac{C_N}{L}\frac{\partial U}{\partial \xi}\ ,\quad \frac{\partial^2 C}{\partial x^2}=\frac{C_N}{L^2}\frac{\partial^2 U}{\partial \xi^2} \tag{3.8}$$

Substituting (3.8) into (3.6) yields

$$\frac{C_N}{T}\frac{\partial U}{\partial \tau}=\frac{D_xC_N}{L^2}\frac{\partial^2 U}{\partial \xi^2}-\frac{vC_N}{L}\frac{\partial U}{\partial \xi}-k_1(UC_N-(C_0-C_{al}))$$

$$\frac{\partial U}{\partial \tau}=\frac{D_xC_NT}{C_NL^2}\frac{\partial^2 U}{\partial \xi^2}-\frac{vTC_N}{C_NL}\frac{\partial U}{\partial \xi}-\frac{k_1TUC_N}{C_N}+\frac{k_1T(C_0-C_{al})}{C_N}$$

$$\frac{\partial U}{\partial \tau}=\frac{D_xT}{L^2}\frac{\partial^2 U}{\partial \xi^2}-\frac{vT}{L}\frac{\partial U}{\partial \xi}-k_1TU+\frac{k_1T(C_0-C_{al})}{C_N} \tag{3.9}$$

Let $$a=\frac{D_xT}{L^2}\ ,\quad b=\frac{vT}{L}\ ,\quad M=k_1T\ ,\quad P=\frac{(C_0-C_{al})}{C_N}$$

The equation (3.9) becomes

$$\frac{\partial U}{\partial \tau}=a\frac{\partial^2 U}{\partial \xi^2}-b\frac{\partial U}{\partial \xi}-M(U-P) \tag{4.0}$$

The initial condition is $U(\xi,0) = C_0,\ 0 \le \xi \le 1$ and the boundary conditions are

$$U(0,\tau) = C_1,\ \ \tau > 0 \ \text{ and } \ \frac{\partial U(L,\tau)}{\partial \xi} = 0, \ \text{for all } \xi,\ x \text{ and } \tau$$

3.3 Numerical Solution by Crank – Nicolson Implicit Method

In this section we approximate function $U(\xi,\tau)$ from (4.0) using finite different method. The function $U(\xi,\tau)$ has independent variable ξ and τ, then mesh point $\xi - \tau$ forms coordinate rectangular. Let the distance step size ξ is $\Delta\xi = h$ and the time steps size τ is $\Delta\tau = k$, we determine $\xi_i = ih$ whereas $i = 1,2,3...,N$ and $\tau_j = jk$ whereas $j = 1,2,3,...,M$

We approximate partial differential equation of $U(\xi,\tau)$ by Crank – Nicolson implicit method from (4.1).

$$\frac{\partial^2 U}{\partial \xi^2} \simeq \frac{1}{2}\left(\frac{U_{i+1,j+1} - 2U_{i,j+1} + U_{i-1,j+1}}{h^2} + \frac{U_{i+1,j} - 2U_{i,j} + U_{i-1,j}}{h^2}\right) \tag{4.1}$$

and approximate first order differential of $U(\xi,\tau)$ by central finite difference, we have

$$\frac{\partial U}{\partial \xi} \simeq \frac{U_{i+1,j} - U_{i-1,j}}{2h} \tag{4.2}$$

$$\frac{\partial U}{\partial \tau} \simeq \frac{U_{i,j+1} - U_{i,j}}{k} \tag{4.3}$$

We approximate partial differential by Crank – Nicolson implicit method and central finite different with (4.2) and (4.3) by corresponding with the initial condition and the boundary conditions. Substituting (4.1), (4.2) and (4.3) into (4.0), we have

$$\frac{U_{i,j+1} - U_{i,j}}{k} = \frac{a}{2}\left(\frac{U_{i+1,j+1} - 2U_{i,j+1} + U_{i-1,j+1}}{h^2} + \frac{U_{i+1,j} - 2U_{i,j} + U_{i-1,j}}{h^2}\right) - b\left(\frac{U_{i+1,j} - U_{i-1,j}}{2h}\right) - M(U_{i,j} - P)$$

$$\frac{2h^2\left(U_{i,j+1} - U_{i,j}\right)}{k} = aU_{i+1,j+1} - 2aU_{i,j+1} + aU_{i-1,j+1} + aU_{i+1,j} - 2aU_{i,j} + aU_{i-1,j} - bhU_{i+1,j} + bhU_{i-1,j} - 2h^2M(U_{i,j} - P)$$

Let $r = k/h^2$

$$2U_{i,j+1} - 2U_{i,j} = raU_{i+1,j+1} - 2raU_{i,j+1} + arU_{i-1,j+1} + raU_{i+1,j} - 2raU_{i,j} + raU_{i-1,j} - rbhU_{i+1,j} + rbhU_{i-1,j} - 2rh^2M(U_{i,j} - P)$$

$$-raU_{i+1,j+1} + (2+2ra)U_{i,j+1} - raU_{i-1,j+1} = (ra - brh)U_{i+1,j} - (2ra - 2 + 2Mrh^2)U_{i,j} + (ra + brh)U_{i-1,j} + 2Mrh^2P \qquad (4.4)$$

From (4.4), we determine new variables to simplify form.

$$A = -ra, \qquad B = (2+2ra), \qquad O = -ra, \qquad D = (ra - bhr)$$

$$E = -(2ra - 2 + 2Mrh^2), \qquad F = (ra + brh), \qquad G = 2Mrh^2$$

Thus (4.4) becomes

$$AU_{i+1,j+1} + BU_{i,j+1} + OU_{i-1,j+1} = DU_{i+1,j} + EU_{i,j} + FU_{i-1,j} + GP \qquad (4.5)$$

In research we mesh point ξ for N points and let $U_{1,j}$ and $U_{N,j}$ whereas $j = 0,1,2,\dots,M$ is the boundary of this problem. We determine the boundary is C_0 for corresponding with (4.0).

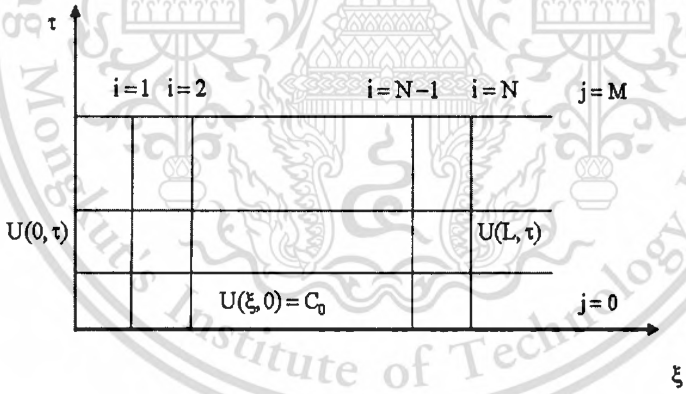

Fig. 3.1 Mesh point for computation numerical solution of (4.5)

We mesh point on ξ axis, it occur $N-2$ equations and $N-2$ unknown variables. When we mesh point $M+1$ on τ axis whereas $j = 0,1,2,\dots,M$, we consider row $j = 0$ thus $U_{i,0}$ when $i = 1,2,\dots,N$.

Substituting $i = 1,2,3,\dots,N$ and $j = 0,1,2,\dots,M$ into the boundary conditions.

Whereas $i = 1,\ j = 0$, we obtain

$$AU_{2,1} + BU_{1,1} + OU_{0,1} \quad = \quad DU_{2,0} + EU_{1,0} + FU_{0,0} + GP$$

$$AU_{2,1} + BU_{1,1} \quad = \quad DU_{2,0} + EU_{1,0} + FU_{0,0} + GP - OU_{0,1} \tag{4.6}$$

$i = 2, \quad j = 0$;

$$AU_{3,1} + BU_{2,1} + OU_{1,1} \quad = \quad DU_{3,0} + EU_{2,0} + FU_{1,0} + GP \tag{4.7}$$

$\vdots$

$i = N-1, \quad j = 0;$

$$AU_{N-2,1} + BU_{N-1,1} + OU_{N,1} \quad = \quad DU_{N-2,0} + EU_{N-1,0} + FU_{N,0} + GP$$

$$AU_{N-2,1} + BU_{N-1,1} \quad = \quad DU_{N-2,0} + EU_{N-1,0} + FU_{N,0} + GP(N-1) - O\left(U_{N-1,1}\right)$$

$$AU_{N-2,1} + BU_{N-1,1} + OU_{N-1,1} \quad = \quad DU_{N-2,0} + EU_{N-1,0} + FU_{N,0} + GP$$

$$AU_{N-2,1} + (B+O)U_{N-1,1} \quad = \quad DU_{N-2,0} + EU_{N-1,0} + FU_{N,0} + GP \tag{4.8}$$

We show equation (4.9) of tridiagonal system, we obtain

$$\begin{bmatrix} B & O & & & & & & \\ A & B & O & & & & & \\ & A & B & O & & & & \\ & & \cdot & \cdot & \cdot & & & \\ & & & \cdot & \cdot & \cdot & & \\ & & & & \cdot & \cdot & \cdot & \\ & & & & & A & B & O \\ & & & & & & A & (B+O) \end{bmatrix} \begin{bmatrix} U_{1,1} \\ U_{2,1} \\ U_{3,1} \\ U_{4,1} \\ \vdots \\ \\ \\ U_{N-1,1} \end{bmatrix} = \begin{bmatrix} E & F & & & & & & \\ D & E & F & & & & & \\ & D & E & F & & & & \\ & & \cdot & \cdot & \cdot & & & \\ & & & \cdot & \cdot & \cdot & & \\ & & & & \cdot & \cdot & \cdot & \\ & & & & & D & E & F \\ & & & & & & D & E \end{bmatrix} \begin{bmatrix} U_{1,0} \\ U_{2,0} \\ U_{3,0} \\ U_{4,0} \\ \vdots \\ \\ \\ U_{N-1,0} \end{bmatrix}$$

$$+\begin{bmatrix} GP + FU_{0,0} - OU_{0,1} \\ GP \\ GP \\ GP \\ \vdots \\ \\ FU_{N,0} + GP \end{bmatrix} \qquad (4.9)$$

From matrix of (4.9), we simplify $AX = B$.

$$A = \begin{bmatrix} B & O & & & & & \\ A & B & O & & & & \\ & A & B & O & & & \\ & & \cdot & \cdot & \cdot & & \\ & & & \cdot & \cdot & \cdot & \\ & & & & \cdot & \cdot & \cdot \\ & & & & A & B & O \\ & & & & & A & (B+O) \end{bmatrix}, \qquad X = \begin{bmatrix} C^*_{1,1} \\ C^*_{2,1} \\ C^*_{3,1} \\ C^*_{4,1} \\ \vdots \\ \\ C^*_{N-1,1} \end{bmatrix}$$

$$B = \begin{bmatrix} E & F & & & & & \\ D & E & F & & & & \\ & D & E & F & & & \\ & & \cdot & \cdot & \cdot & & \\ & & & \cdot & \cdot & \cdot & \\ & & & & \cdot & \cdot & \cdot \\ & & & & D & E & F \\ & & & & & D & E \end{bmatrix} \begin{bmatrix} C^*_{1,0} \\ C^*_{2,0} \\ C^*_{3,0} \\ C^*_{4,0} \\ \vdots \\ \\ C^*_{N-1,0} \end{bmatrix} + \begin{bmatrix} GP + FC^*_{0,0} - OC^*_{0,1} \\ GP \\ GP \\ GP \\ \vdots \\ \\ FC^*_{N,0} + GP \end{bmatrix}$$

From matrix of (4.9), equation of system is solved by $X = A^{-1}B$ and using MATLAB program for computing and showing graphic. We have to show in next chapter 4.

3.4 Steady State Solution

The concept of steady state relates to the absence of changes in a system. An important question stemming from many problems in the natural sciences is whether constant solutions representing these static situations exist.

In some cases steady state solutions are of intrinsic interest: for example, most living organisms function well in rather narrow ranges of temperature, acidity, or salinity. (More highly evolved organisms have developed intricate internal mechanisms for maintaining body temperatures and other factors at their appropriate constant levels.) On the other hand, steady state solutions may seem of marginal interest in problems involving dynamic events such as growth, propagation, or reproduction of a population [5].

Nevertheless, it is often true that by examining carefully what happens in a steady state. Then in this section we use (4.0) for solving steady state solution.

From (4.0) we solve steady state solution by defining $\frac{\partial U}{\partial \tau} = 0$, we obtain:

$$a\frac{d^2U}{d\xi^2} - b\frac{dU}{d\xi} - MU = -MP \tag{5.0}$$

The equation (5.0) is nonhomogeneous ordinary differential equation. Thus, the general solution is formed as a sum of homogeneus $U_h(x)$ and a particular solution $U_p(x)$ solution. We can to show that in this form:

$$U(x) = U_h(x) + U_p(x)$$

In the first of solving (5.0), we start to solve homogeneous form,

$$a\frac{d^2U}{d\xi^2} - b\frac{dU}{d\xi} - MU = 0 \qquad (5.1).$$

The equation (5.1) is characteristic equation form so we decide $\frac{dU}{d\xi} = r$ for solving solution of (5.1).

We have

$$ar^2 - br - M = 0.$$

Hence, the roots of above equation are:

$$r_1 = \frac{b+\sqrt{b^2+4aM}}{2a}$$

$$r_2 = \frac{b-\sqrt{b^2+4aM}}{2a} \tag{5.2}$$

From (5.2), we consider solution of homogeneous ordinary equation into 3 cases.

case 1. If $b^2+4aM=0$ then $r_{1,2} = \dfrac{b}{2a}$

therefore, the solution in this case is form $U_h(\xi) = A_1 e^{\left(\frac{b}{2a}\right)\xi} + A_2 \xi e^{\left(\frac{b}{2a}\right)\xi}$.

case 2. If $b^2+4aM>0$ then $r_1 = \dfrac{b+\sqrt{b^2+4aM}}{2a}$, $r_2 = \dfrac{b-\sqrt{b^2+4aM}}{2a}$

therefore, the solution in case 2 is form $U_h(\xi) = A_1 e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)\xi} + A_2 e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)\xi}$.

case 3. If $b^2+4aM<0$ in this case has no solution because each parameter is positive.

We guess that a particular solution to (5.0) is a polynomial,

$$\begin{aligned} U_p(\xi) &= A\xi^2 + B\xi + D \\ U_p'(\xi) &= 2A\xi + B \\ U_p''(\xi) &= 2A \end{aligned} \tag{5.3}$$

we substitute (5.3) into (5.0), we have:

$$a(2A) - b(2A\xi + B) - M(A\xi^2 + B\xi + D) + MP = 0$$

then A and B are equal zero, we obtain:

$$\begin{aligned} -MD + MP &= 0 \\ -MD &= -MP \\ D &= P \end{aligned}$$

then, a particular solution $U_P(\xi) = P$.

Therefore, from the general solution we have:

case 1. If $b^2+4aM=0$

therefore, the solution in this case is form $U(\xi) = A_1 e^{\left(\frac{b}{2a}\right)\xi} + A_2 \xi e^{\left(\frac{b}{2a}\right)\xi} + P$.

case 2. If $b^2+4aM>0$

therefore, the solution in case 2 is form $U(\xi) = A_1 e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)\xi} + A_2 e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)\xi} + P$.

Next, we solve for arbitrary constant from boundary condition

$$U(0)=C_1 \text{ and } \frac{\partial U(L,\tau)}{\partial \xi} = 0,$$

we obtain:

Case 1. $U(\xi)=A_1e^{\left(\frac{b}{2a}\right)\xi}+A_2\xi e^{\left(\frac{b}{2a}\right)\xi}+P$

whereas $\xi=0$

$$\begin{aligned} U(0) &= A_1e^{\left(\frac{b}{2a}\right)0}+A_2 0e^{\left(\frac{b}{2a}\right)0}+P \\ C_1 &= A_1+P \\ A_1 &= C_1-P \end{aligned}$$

whereas $\xi=L$

$$U'(\xi)=A_1\left(\frac{b}{2a}\right)e^{\left(\frac{b}{2a}\right)\xi}+A_2\left(\left(\frac{b}{2a}\right)\xi e^{\left(\frac{b}{2a}\right)\xi}+e^{\left(\frac{b}{2a}\right)\xi}\right)$$

$$U'(L)=(C_1-P)\left(\frac{b}{2a}\right)e^{\left(\frac{b}{2a}\right)L}+A_2\left(\left(\frac{b}{2a}\right)Le^{\left(\frac{b}{2a}\right)L}+e^{\left(\frac{b}{2a}\right)L}\right)$$

$$0=(C_1-P)\left(\frac{b}{2a}\right)e^{\left(\frac{b}{2a}\right)L}+A_2\left(\left(\frac{b}{2a}\right)Le^{\left(\frac{b}{2a}\right)L}+e^{\left(\frac{b}{2a}\right)L}\right)$$

$$A_2=\frac{-(C_1-P)\left(\frac{b}{2a}\right)e^{\left(\frac{b}{2a}\right)L}}{\left(\frac{b}{2a}\right)Le^{\left(\frac{b}{2a}\right)L}+e^{\left(\frac{b}{2a}\right)L}}$$

therefore solution of case 1. is $U(\xi)=(C_1-P)e^{\left(\frac{b}{2a}\right)\xi}+\left(\frac{(C_1-P)\left(\frac{b}{2a}\right)e^{\left(\frac{b}{2a}\right)L}}{\left(\frac{b}{2a}\right)Le^{\left(\frac{b}{2a}\right)L}+e^{\left(\frac{b}{2a}\right)L}}\right)\xi e^{\left(\frac{b}{2a}\right)\xi}+P$

(5.4).

Case 2. $U(\xi)=A_1e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)\xi}+A_2e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)\xi}+P$

whereas $\xi=0$

$$\begin{aligned} U(0) &= A_1e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)0}+A_2e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)0}+P \\ C_1 &= A_1+A_2+P \\ A_1 &= C_1-A_2-P \end{aligned}$$

whereas $\xi = L$

$$U'(L) = A_1\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L} + A_2\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)L}$$

$$0 = (C_1 - A_2 - P)\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L} + A_2\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)L}$$

$$-(C_1 - P)\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L} =$$

$$\left(\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)L} - \left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}\right)A_2$$

$$A_2 = \frac{-(C_1 - P)\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}}{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)L} - \left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}}$$

therefore solution of case 2. is

$$\begin{aligned} U(\xi) = {} & \left(C_1 - \left(\frac{-(C_1 - P)\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}}{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)L} - \left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}}\right) - P\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)\xi} \\ & + \left(\frac{-(C_1 - P)\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}}{\left(\frac{b-\sqrt{b^2+4ak_1T}}{2a}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)L} - \left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)e^{\left(\frac{b+\sqrt{b^2+4aM}}{2a}\right)L}}\right)e^{\left(\frac{b-\sqrt{b^2+4aM}}{2a}\right)\xi} + P. \end{aligned} \tag{5.5}$$

We show the solution of steady state in 2 cases of (5.4) and (5.5). Next chapter, we show behavior of these equation by using MALAB program.

Next, we solve analytical solution by using Similarity. The Similarity Method is a method for solving parabolic equation form of partial differential equation. Then we format (3.1) to simply form.

Let $C^{*}=C-C_{0}+C_{al}$, the equation (3.1) becomes:

$$\frac{\partial C^{*}}{\partial t}=D_{x}\frac{\partial^{2}C^{*}}{\partial x}-v\frac{\partial C^{*}}{\partial x}-kC^{*} \tag{5.6}$$

The similarity method has techniques for solving partial differential equation by using similarity methods such as Free Parameter Method, Separation of Variables Method, Group Theory Method and Dimensional Analysis Method. Among these methods, we consider to apply the group theory technique of similarity methods for solving (5.6).

3.5 Similarity Analysis by Invariance Groups

3.5.1 The Analysis of Invariance

This is the first part of finding the analytical solution.

Let

$$\left.\begin{aligned}&T=a^{n}t\Rightarrow t=a^{-n}T\\&X=a^{m}x\Rightarrow x=a^{-m}X\\&C=a^{p}C^{*}\Rightarrow C^{*}=a^{-p}C\end{aligned}\right\} \tag{5.7}$$

where T, X, and C are functions of t, x and C^{*}, respectively; a is an variable and m, n, p are the parameters.

Substituting the parameter group of the transformation (5.7) into (5.6), we have

$$\begin{aligned}\frac{\partial C^{*}}{\partial t}-D_{x}\frac{\partial^{2}C^{*}}{\partial x^{2}}+v\frac{\partial C^{*}}{\partial x}+kC^{*}&=\frac{a^{-p}}{a^{-n}}\frac{\partial C}{\partial T}-\frac{D_{x}a^{-p}}{a^{-2m}}\frac{\partial^{2}C}{\partial X^{2}}+\frac{va^{-p}}{a^{-m}}\frac{\partial C}{\partial X}+ka^{-p}C\\&=a^{-p+n}\frac{\partial C}{\partial T}-D_{x}a^{-p+2m}\frac{\partial^{2}C}{\partial X^{2}}+va^{-p+m}\frac{\partial C}{\partial X}+ka^{-p}C\end{aligned} \tag{5.8}$$

Equating the powers of a yields

$$-p+n=-p+2m=-p+m=-p$$

Let $-p+2m=-p+m\Rightarrow m=0$

$$-p+n=-p+m \Rightarrow m=0,\ n=0$$

which provides the zero values of m and n. Then (5.8) becomes

$$\frac{\partial C^*}{\partial t}-D_x\frac{\partial^2 C^*}{\partial x^2}+v\frac{\partial C^*}{\partial x}+kC^*=a^{-p}\left[\frac{\partial C}{\partial T}-\frac{\partial^2 C}{\partial X^2}+\frac{\partial C}{\partial X}+kC\right]$$

Note that if $p\equiv 0$ then the equation will reduce into the constant conformally invariant.

3.5.2 Similarity Solution

This section is the second part of finding the analytical solution by using Similarity Method [10].

Let $\eta = xt^s$

By applying the parameter group of transformation and employing the constant conformally invariants

$$\eta = xt^s=(a^{-m}X)(a^{-n}T)^s=a^{-m-ns}.XT^s$$

And then $\eta = xt^{-\left(\frac{m}{n}\right)}$

where $s=\dfrac{-m}{n}$

Next, we define function which is the function $g=C^*(x,t)t^r$ of the dependent variable $C^*(x,t)$ as well as the independent variable t.

$$g=(a^{-p}C(x,t))(a^{-n}T)^r=a^{-p-nr}C(x,t)T^r$$

Similarly, we have

$$g=C^*(x,t)t^{\frac{-p}{n}}$$

and then $g=C^*(x,t)t^{\frac{-p}{n}}\equiv F(\eta)$

where g is defined to be the function of η in the last equality.

$$C^*(x,t) = F(\eta)t^{\frac{p}{n}} \qquad (*)$$

Which we can change (5.6) with two independent variable x and t to (5.6) with just one variable, η, as the following ateps.

First, we differentiate (*) with respect to x and t ;

$$\frac{\partial C^*}{\partial t} = \frac{pt^{\frac{p}{n}-1}}{n}F(\eta) + t^{\frac{p}{n}}F'(\eta)\left(\frac{-m}{n}\right)xt^{\frac{-m}{n}-1} = t^{\frac{p}{n}-1}\left(\frac{pF(\eta)}{n} - \frac{m\eta F'(\eta)}{n}\right) \qquad (5.9)$$

$$\frac{\partial C^*}{\partial x} = t^{\frac{p}{n}}F'(\eta)t^{-\frac{m}{n}} = t^{\frac{p}{n}-\frac{m}{n}}F'(\eta) \qquad (6.0)$$

$$\frac{\partial^2 C^*}{\partial x^2} = t^{\frac{p}{n}-\frac{m}{n}}F''(\eta)t^{-\frac{m}{n}} = t^{\frac{p}{n}-\frac{2m}{n}}F''(\eta) \qquad (6.1)$$

and then substitute (5.9), (6.0) and (6.1) into (5.6), can be written:

$$t^{\frac{p}{n}-1}\left(\frac{pF(\eta)}{n} - \frac{m\eta F'(\eta)}{n}\right) - D_x t^{\frac{p}{n}-\frac{2m}{n}}F''(\eta) + vt^{\frac{p}{n}-\frac{m}{n}}F'(\eta) + kF(\eta)t^{\frac{p}{n}} = 0$$

Next, equating the power of t, we have

$$-\left(\frac{p}{n}-1\right) = -\left(\frac{p}{n}-\frac{2m}{n}\right) = -\left(\frac{p}{n}-\frac{m}{n}\right) = -\frac{p}{n} \quad \text{for } (n \neq 0)$$

$$t^{-\left(\frac{p}{n}-1\right)}\left\{\left(\frac{p}{n}+k\right)F(\eta) - \left(\frac{m\eta}{n}-v\right)F'(\eta) - D_xF''(\eta)\right\} = 0$$

Thus;
$$\left(\frac{p}{n}+k\right)F(\eta) - \left(\frac{m\eta}{n}-v\right)F'(\eta) - D_xF''(\eta) = 0 \qquad (6.2)$$

We consider:

1).If $\frac{p}{n}-1=0 \Rightarrow \frac{p}{n}=1$ & $\frac{p}{n}-\frac{2m}{n}=0$ then $\frac{p}{n}=\frac{2m}{n} \Rightarrow \frac{m}{n}=\frac{1}{2}$ (6.2a)

2).If $\frac{p}{n}-1=0 \Rightarrow \frac{p}{n}=1$ & $\frac{p}{n}-\frac{m}{n}=0$ then $\frac{m}{n}=1$ (6.2b)

We choose case 2). then (6.2) becomes:

$$D_xF''(\eta) + (\eta - v)F'(\eta) - (1+k)F(\eta) = 0 \qquad (6.3)$$

It is not difficult to see that the general solution of the second – order ordinary differential equation in the (6.3) is

$$F(\eta) = c_1 F_1(\eta) + c_2 F_2(\eta)$$

we assume the solution (6.3) form $F(\eta) = e^{a\eta}$

thus, $F'(\eta) = ae^{a\eta}$

$F''(\eta) = a^2 e^{a\eta}$

Substituting $F(\eta)$, $F'(\eta)$, $F''(\eta)$ into (6.3), we have:

$$D_x a^2 e^{a\eta} + (\eta - v) a e^{a\eta} - (1+k) e^{a\eta} = 0$$

$$e^{a\eta}\left(D_x a^2 + (\eta - v) a - (1+k)\right) = 0 \qquad , e^{a\eta} \neq 0$$

$$a^2 + \frac{(\eta - v)}{D_x} a - \frac{(1+k)}{D_x} = 0$$

$$\therefore \quad a = -\frac{(\eta - v)}{2D_x} \pm \frac{1}{2}\sqrt{\left(\frac{(\eta - v)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}$$

We have:

$$F(\eta) = c_1 e^{\left(-\frac{(\eta-v)}{2D_x} + \frac{1}{2}\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}\right)\eta} + c_2 e^{\left(-\frac{(\eta-v)}{2D_x} - \frac{1}{2}\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}\right)\eta}$$

The boundary condition form $C^*(0,t) = A_1$, $\frac{\partial C^*}{\partial x}(L,t) = 0$

and the initial condition $C^*(x,0) = C_0$

whereas $C^*(x,t) = (C(x,t) - C_0 + C_{al})$ $\quad , C^*(x,t)t^{-\frac{p}{n}} = F(\eta)$ $\quad , \eta = xt^{-\frac{m}{n}}$

We convert the initial condition and the boundary conditions to the value of $F(\eta)$

The initial condition $\quad C^*(x,0)t^{-\frac{p}{n}} = F(\eta(x,0)) = C_0 \cdot (0)^{-\frac{p}{n}} \quad , 0 < \frac{p}{n} < \infty$

$$\therefore \quad F(\eta(x,0)) = 0$$

and the boundary conditions $\quad C^{*}(0,t)t^{-\frac{p}{n}} = A_1 t^{-\frac{p}{n}} = F(\eta(0,t)) = 0$

$$(C(0,t) - C_0 + C_{al})t^{-\frac{p}{n}} = 0 \quad , \quad t^{-\frac{p}{n}} \neq 0$$

$$\therefore \quad F(\eta(0,t)) = (A_1 - C_0 + C_{al})t^{-\frac{p}{n}} \quad , \quad t > 0$$

$$\frac{\partial C^{*}(L,t)}{\partial x} = \frac{\partial C^{*}(L,t)}{\partial \eta} \cdot \frac{\partial \eta}{\partial x} = t^{-\frac{m}{n}} \cdot \frac{\partial C^{*}(L,t)}{\partial \eta} = 0$$

$$t^{-\frac{p}{n}} \frac{\partial C^{*}(L,t)}{\partial \eta} = 0$$

$$\therefore \quad \frac{\partial F(\eta)}{\partial \eta} = 0 \quad , \quad \forall_{x,t}$$

From $\quad \eta = xt^{-\left(\frac{m}{n}\right)}$ we have:

$$F(\eta(x,t)) = c_1 e^{\left(-\frac{\left(xt^{-\left(\frac{m}{n}\right)} - v\right)}{2D_x} + \frac{1}{2}\sqrt{\left(\frac{\left(xt^{-\left(\frac{m}{n}\right)} - v\right)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}\right) xt^{-\left(\frac{m}{n}\right)}} + c_2 e^{\left(-\frac{\left(xt^{-\left(\frac{m}{n}\right)} - v\right)}{2D_x} - \frac{1}{2}\sqrt{\left(\frac{\left(xt^{-\left(\frac{m}{n}\right)} - v\right)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}\right) xt^{-\left(\frac{m}{n}\right)}}$$

To find the arbitrary constants, we obtain:

whereas $F(\eta(0,t)) = (A_1 - C_0 + C_{al})t^{-\frac{p}{n}} , \quad t > 0$

$$F(\eta(0,t)) = c_1 e^{\left(-\frac{\left(0.t^{\frac{-m}{n}} - v\right)}{2D_x} + \frac{1}{2}\sqrt{\left(\frac{\left(0.t^{\frac{-m}{n}} - v\right)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}\right) 0.t^{\frac{-m}{n}}} + c_2 e^{\left(-\frac{\left(0.t^{\frac{-m}{n}} - v\right)}{2D_x} - \frac{1}{2}\sqrt{\left(\frac{\left(0.t^{\frac{-m}{n}} - v\right)}{D_x}\right)^2 + \frac{4(1+k)}{D_x}}\right) 0.t^{\frac{-m}{n}}}$$

$$(A_1 - C_0 + C_{al})t^{-\frac{p}{n}} = c_1 + c_2$$

$$\therefore \quad c_2 = (A_1 - C_0 + C_{al})t^{-\frac{p}{n}} - c_1$$

and $\dfrac{\partial F(\eta(L,t))}{\partial \eta} = 0 \quad , \quad \forall_{x,t}$

$$\frac{\partial F(\eta(L,t))}{\partial \eta} = c_1\left(\left(\frac{(\eta-v)}{2D_x^2\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\frac{1}{2D_x}\right)e^{\left(\left(\frac{-(\eta-v)}{2D_x}\right)+\frac{1}{2}\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)\eta}\right)$$

$$+c_2\left(\left(\frac{-(\eta-v)}{2D_x^2\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\frac{1}{2D_x}\right)e^{\left(\left(\frac{-(\eta-v)}{2D_x}\right)-\frac{1}{2}\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)\eta}\right)$$

$$0 = \left(\begin{array}{l} c_1\left(\dfrac{(Lt^{-\frac{m}{n}}-v)}{2D_x^2\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\dfrac{1}{2D_x}\right)e^{\left(\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x}\right)+\frac{1}{2}\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)Lt^{-\frac{m}{n}}} \\ +\left((A_I-C_0+C_{al})t^{-\frac{p}{n}}-c_1\right)\left(\dfrac{-(Lt^{-\frac{m}{n}}-v)}{2D_x^2\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\dfrac{1}{2D_x}\right)e^{\left(\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x}\right)-\frac{1}{2}\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)Lt^{-\frac{m}{n}}} \end{array}\right)$$

$$0 = c_1\left(\left(\frac{(Lt^{-\frac{m}{n}}-v)}{2D_x^2\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\frac{1}{2D_x}\right)e^{\left(\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x}\right)+\frac{1}{2}\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)Lt^{-\frac{m}{n}}} + \left((A_1-C_0+C_{al})t^{-\frac{p}{n}}-1\right)\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x^2\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\frac{1}{2D_x}\right)e^{\left(\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x}\right)-\frac{1}{2}\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)Lt^{-\frac{m}{n}}}\right)$$

$$c_1 = \frac{0}{\left(\left(\frac{(Lt^{-\frac{m}{n}}-v)}{2D_x^2\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\frac{1}{2D_x}\right)e^{\left(\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x}\right)+\frac{1}{2}\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)Lt^{-\frac{m}{n}}} + \left((A_1-C_0+C_{al})t^{-\frac{p}{n}}-1\right)\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x^2\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}}-\frac{1}{2D_x}\right)e^{\left(\left(\frac{-(Lt^{-\frac{m}{n}}-v)}{2D_x}\right)-\frac{1}{2}\sqrt{\left(\frac{(Lt^{-\frac{m}{n}}-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)Lt^{-\frac{m}{n}}}\right)}$$

$\therefore \quad c_1 = 0$ thus $c_2 = (A_1 - C_0 + C_{al})t^{-\frac{p}{n}}$

The general solution is form:

$$F(\eta) = 0.e^{\left(-\frac{(\eta-v)}{2D_x}+\frac{1}{2}\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)\eta} + \left((A_1-C_0+C_{al})t^{-\frac{p}{n}}\right)\cdot e^{\left(-\frac{(\eta-v)}{2D_x}-\frac{1}{2}\sqrt{\left(\frac{(\eta-v)}{D_x}\right)^2+\frac{4(1+k)}{D_x}}\right)\eta}$$ From

$C^*(x,t)t^{-\left(\frac{p}{n}\right)} = F(\eta)$ and $C^*(x,t) = (C(x,t) - C_0 + C_{al})$ we obtain:

$$C(x,t)=t^{\frac{p}{n}}\left((A_1-C_0+C_{al})t^{-\frac{p}{n}}\right)\cdot e^{\left(\frac{\left(xt^{-\left(\frac{m}{n}\right)}-v\right)}{2D_x}-\frac{1}{2}\sqrt{\left(\frac{\left(xt^{-\left(\frac{m}{n}\right)}-v\right)}{D_x}\right)^2+\frac{4(1+k)}{D_x}xt^{-\left(\frac{m}{n}\right)}}\right)}+C_0-C_{al}$$

or

$$C(x,t)=(A_1-C_0+C_{al})\cdot e^{\left(-\frac{\left(xt^{-\left(\frac{m}{n}\right)}-v\right)}{2D_x}-\frac{1}{2}\sqrt{\left(\frac{\left(xt^{-\left(\frac{m}{n}\right)}-v\right)}{D_x}\right)^2+\frac{4(1+k)}{D_x}xt^{-\left(\frac{m}{n}\right)}}\right)}+C_0-C_{al} \qquad (6.4)$$

Next chapter we show graphs of numerical solution, steady state and analytical solution. That we use experimental data for graphing of these results.

Chapter 4

Numerical, Steady State and Analytical Results

In this chapter we will show results of numerical, steady state and analysis solutions by using MATLAB program for finding the remaining concentrations of metals in the contaminated wastewater at any time and various distances.

4.1 Numerical Result

We use experimental data of the adsorption of malachite green onto *Phithophora sp.* [4]. and show the numerical results at any time and various distances by Fig. 4.1

$$D_{w} = 0.1\left[m^2/\min\right], \qquad v = 0.1\left[m/s\right], \qquad C_{ab} = 64\left[mg/l\right],$$
$$k_1 = 1.42\left[1/\min\right], \qquad C_0 = 100\left[mg/l\right]$$

We compute the point of x and t axis of (5.1). We have the matrix size of 11×11, then we display the graph of numerical solution.

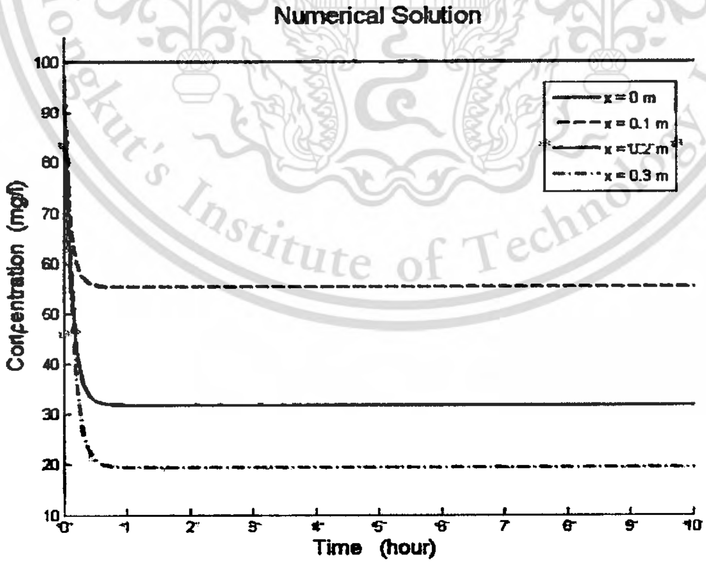

Fig.4.1 shows numerical solutions of the remaining concentration of metals in the contaminated wastewater at any time and various distances.

Table 4.1 Data of concentration of metals in the contaminated wastewater by numerical computation.

t x	0	1	2	3	4	5	6	7	8	9	10
0	100	100	100	100	100	100	100	100	100	100	100
0.1	100	67.58	59.92	58.12	57.69	57.57	57.56	57.56	57.56	57.56	57.56
0.2	100	60.21	42.83	36.84	34.98	34.44	34.29	34.25	34.23	34.23	34.23
0.3	100	57.16	36.48	27.14	23.42	22.07	21.61	21.47	21.42	21.41	21.41

We approximate the remaining of concentration of metals in the contaminated wastewater by Crank – Nicolson implicit method. The result shows any distance asymptotically reaches the equilibrium state.

4.2 Steady State Result

In this section we use experimental data of the adsorption of dye onto *Phithophora sp.* [4] for showing behavior of steady state results in 2 cases. In case $b^2 + 4aM = 0$ the graph of solution is:

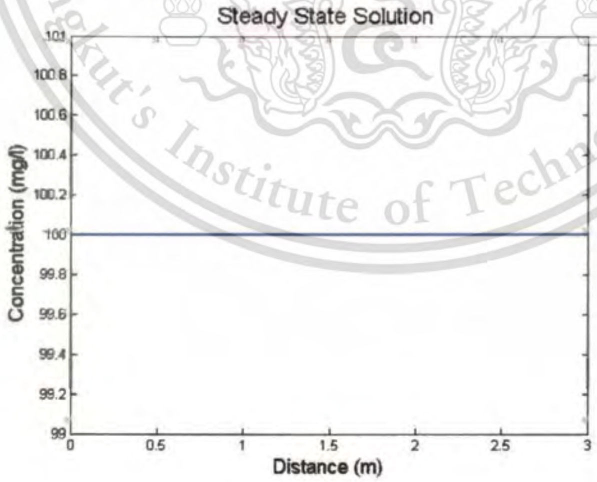

Fig 4.2 shows the solution of steady state in case $b^2 + 4aM = 0$

From the fig 4.2 we decide parameter from experimental data for according with the case of $b^2+4aM=0$. The result shows the concentration of 100 mg/g approaches to infinity. Therefore the graph of this case disagrees our model.

Next we show the result of case $b^2+4aM>0$ and use parameter sames in case of $b^2+4aM=0$, we have:

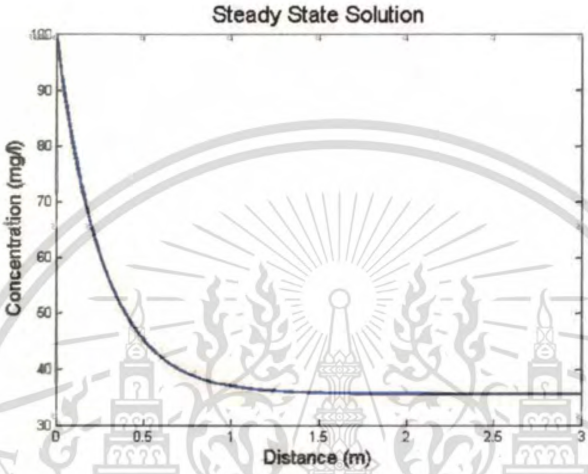

Fig 4.3 shows the solution of steady state in case $b^2+4aM>0$

From fig 4.3 the result shows the remaining of concentration approximately 35. 9 mg/l at steady state. Thus in this case conform with our model.

4.3 Analytical Result

We use experimental data of the adsorption of dye onto *Phithophora sp.*[4] with analytical solution of (6). We show the comparing analytical result from experimental data also with the average analytical result.

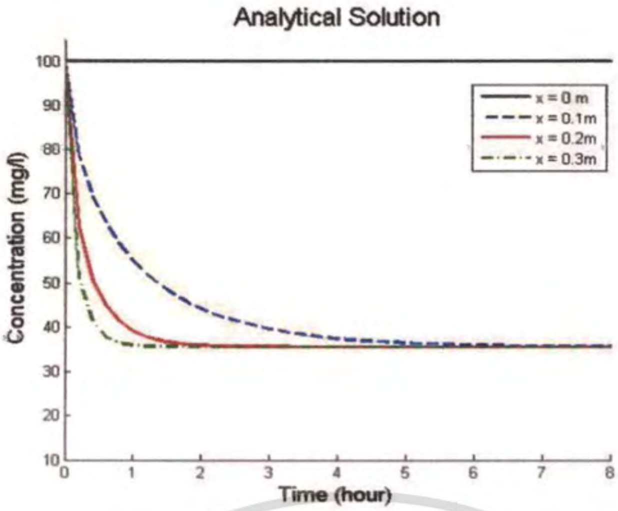

Fig. 4.4 shows the remaining of concentration of dye in water body with analytic solution after adsorption by *Phithophora sp.* The result shows any position decreases and asymptotically reaches the equilibrium state at 35.7 mg/l.

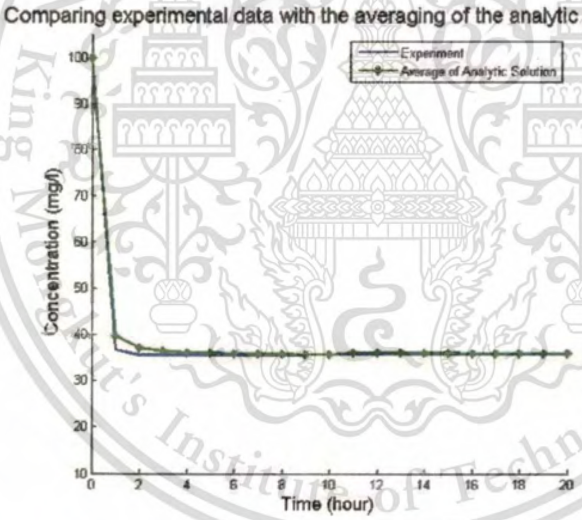

Fig. 4.5 comparing the experiment with average analytic solution found that the experimental result conforms to the average analytic solution and asymptotically reaches the equilibrium state 35.7 mg/l at 50 minutes.

In research [9] studied adsorption of chromium (VI) from electroplating factory by chitosan resin. We use experimental data with analytical solution of equation 6 for comparing the analytic with the average analytical result.

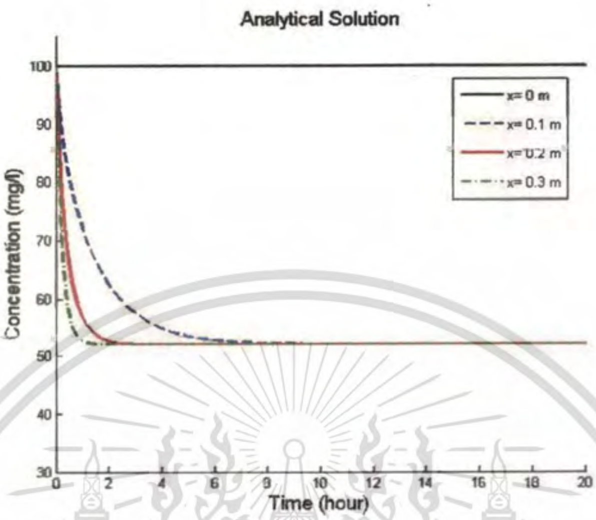

Fig. 4.6 shows the remainder of concentration of chromium (VI) in water body with analytic solution after adsorption by chitosan resin. The result shows decreasing of any position and asymptotically reaches the equilibrium state at 52.2 mg/l.

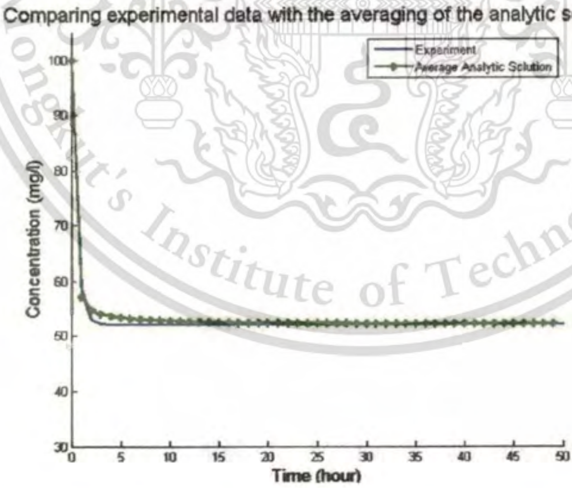

Fig. 4.7 comparing experiment with average analytic solution found that experimental result conform to average analytic solution and asymptotically reaches the equilibrium state 52.2 mg/l at 6 hour.

Chapter 5

Conclusion and Discussion

5.1 Conclusion

In this research we solve numerical solution by Crank – Nicolson implicit method, steady state solution and analytical solution by Similarity method. The proposed three of method results of the remaining concentration of metals contaminated in wastewater with algae showed that the concentrations of contaminated water in mathematical model decrease to equilibrium state in every case. The results from two related papers, chromium adsorption with chitosan resin and dye adsorption by *Phithophora sp.* had been compared with our results. There has been satisfactory agreement between the theoretical mathematical model and experimental data.

5.2 Suggestions for Further Study

In this research we analyze the remaining concentration of metals in the contaminated wastewater in 1 dimension. In the future we suggest analyzing the remaining concentration in 2 dimensions for analysis is careful more than 1 dimension, and developing adsorption term.

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APPENDIX A.

THE RESEARCH PAPERS

การศึกษาความเข้มข้นของมวลสารในแหล่งน้ำด้วยการดูดซับโดยใช้สาหร่าย

พรวิลัย ชาญกิจกรรณ์[1] และ บุษยมาส พิมพ์พรรณชาติ[1,2,*]

[1]หน่วยวิจัยคณิตศาสตร์อุตสาหกรรมและสาขาวิชาคณิตศาสตร์ คณะวิทยาศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง เขตลาดกระบัง กรุงเทพฯ 10520
[2]ศูนย์ความเป็นเลิศทางคณิตศาสตร์ คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล
272 ถนนพระราม6 แขวงพญาไท เขตราชเทวี กรุงเทพฯ 10400
chankitkan_p@hotmail.com, knbusaya@kmitl.ac.th

บทคัดย่อ : ปัญหาการปนเปื้อนมวลสารในแหล่งน้ำส่วนใหญ่เป็นปัญหาที่เกิดขึ้นจากโรงงานอุตสาหกรรม เช่น โรงงานชุบโลหะ โรงงานฟอกสี เป็นต้น ในการกำจัดมวลสารในน้ำเสียผู้วิจัยได้ใช้ผลการทดลองของการกำจัดสีย้อมจากโรงงานฟอกสีที่มีการดูดซับด้วยสาหร่าย Pithophora sp. ซึ่งจุดประสงค์งานวิจัยได้ศึกษาความเข้มข้นของสีย้อมในแหล่งน้ำด้วยกระบวนการดูดซับโดยใช้สาหร่ายดูดซับ โดยงานวิจัยได้มีการสร้างสมการการดูดซับเพื่อหาความเข้มข้นของสีย้อมในแหล่งน้ำที่เวลาใดๆของการดูดซับเนื่องจากการดูดซับที่เกิดขึ้นความเข้มข้นส่วนหนึ่งจะอยู่บนสาหร่าย จึงสรุปได้ว่าความเข้มข้นของมวลสารในแหล่งน้ำจะมีการดูดซับลดลงจนเข้าสู่สภาวะสมดุล

คำสำคัญ : Pithophora sp; การแพร่การพา; สีย้อม; การดูดซับ; สภาวะสมดุล

1 บทนำ

ปัจจุบันประเทศไทยกำลังก้าวเข้าสู่ประเทศอุตสาหกรรม เนื่องจากว่าในภาคอุตสาหกรรมทำรายได้ให้กับประเทศมากกว่าภาคการเกษตรอย่างน้อย 2 เท่าในขณะที่เศรษฐกิจของประเทศก็มีการเจริญเติบโตอย่างรวดเร็ว ปัญหาสิ่งแวดล้อมก็ได้เพิ่มมากขึ้น อาทิเช่น ปัญหามลพิษทางน้ำที่ไม่ได้หยุดอยู่ที่ความสกปรกในรูปบีโอดี แต่ได้ขยายครอบคลุมไปถึงมลภาวะทางน้ำที่เกิดจากมวลสาร สารพิษ และสารอันตรายอื่นๆ เนื่องจากการที่มีโรงงานตั้งเพิ่มขึ้นอันเป็นผลมาจากการขยายตัวของภาคอุตสาหกรรม

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*Corresponding author e-mail : knbusaya@kmitl.ac.th

จากปัญหาด้านการปนเปื้อนมวลสารในแหล่งน้ำทำให้งานวิจัยด้านนี้เป็นที่สนใจและให้ความสำคัญมาก เนื่องจากว่าปัญหาเหล่านี้เมื่อเกิดขึ้นจะส่งผลกระทบต่อคุณภาพชีวิตของประชาชน สัตว์น้ำ และพืชพรรณที่เป็นแหล่งอาหารได้อย่างยาวนาน ซึ่งมวลสารที่ปนเปื้อนในแหล่งน้ำส่วนใหญ่แล้วจะมาจากโรงงานอุตสาหกรรมต่างๆ มวลสารที่มาจากโรงงานอุตสาหกรรมส่วนใหญ่ได้แก่ แคดเมียม ปรอท ตะกั่ว สารหนู ซึ่งถ้าโรงงานอุตสาหกรรมไม่มีการจัดการในเรื่องการบำบัดของเสียก่อนปล่อยสู่แม่น้ำแล้วก็จะส่งผลกระทบต่อประชาชน สัตว์น้ำ และพืชพรรณในบริเวณแหล่งน้ำนั้นเป็นอย่างมาก

ในแต่ละโรงงานอุตสาหกรรมก่อนที่จะมีการปล่อยของเสียสู่แม่น้ำลำคลองนั้น โรงงานจะต้องมีระบบบำบัดของเสียก่อนที่จะปล่อยน้ำทิ้งลงสู่ธรรมชาติ โดยจะมีขั้นตอนและกระบวนการแยกที่แตกต่างกันออกไป เนื่องจากในแต่ละโรงงานจะมีของเสียแต่ละประเภทและในปริมาณที่แตกต่างกัน โดยการบำบัดน้ำเสียนั้นเมื่อน้ำเสียจากแหล่งกำเนิดถูกระบายโดยท่อระบายน้ำเสียเข้าสู่บ่อรวมน้ำเสียตะกอนขนาดใหญ่ เช่น กรวด ทราย จะตกตะกอนรวมไปถึงไขมันก็จะถูกกำจัดโดยการใช้ตะแกรงดักขยะออกไปก่อนที่จะมีการสูบหรือระบายน้ำเสียไปสู่ระบบบ่อบำบัด

ในระบบบ่อบำบัดจะแบ่งออกเป็นระบบต่างๆเช่น

1) ระบบบำบัดแบบบ่อปรับเสถียรที่อาศัยธรรมชาติในการกำจัดสารอินทรีย์ในน้ำเสียซึ่งแบ่งตามลักษณะการทำงานได้ 3 รูปแบบ คือ บ่อแอโรบิก (Aerobic Pond) บ่อแฟคคัลเททีฟ (Facultative Pond) บ่อแอนแอโรบิก (Anaerobic pond) โดยในรูปแบบของระบบบ่อแอโรบิกจะมีแบคทีเรียและสาหร่ายแขวนลอยอยู่

2) ระบบบำบัดแบบบึงประดิษฐ์เป็นระบบบำบัดน้ำเสียที่อาศัยกระบวนการทางธรรมชาติกำลังเป็นที่นิยมมากขึ้นในปัจจุบัน โดยเฉพาะอย่างยิ่งในการใช้ปรับปรุงคุณภาพน้ำทิ้งที่ผ่านการบำบัดแล้วแต่ต้องการลดปริมาณไนโตรเจนและฟอสฟอรัสก่อนระบายออกสู่แหล่งรองรับน้ำทิ้ง

3) ระบบบำบัดแบบยูเอเอสบีเป็นระบบบำบัดน้ำเสียโดยวิธีชีวภาพที่อาศัยจุลินทรีย์ในการย่อยสลายสารอินทรีย์ในน้ำเสีย

จากรูปแบบการบำบัดน้ำเสียจะเห็นได้ว่าการบำบัดแบบบ่อแอโรบิคจะเป็นบ่อที่มีแบคทีเรียและสาหร่ายแขวนลอยอยู่จากกระบวนการการดูดซับสาหร่ายบางชนิดจะมีคุณสมบัติในการกำจัดมวลสารเช่น แคดเมียม ตะกั่ว เหล็ก และอื่นๆที่ถูกปล่อยมาจากโรงงานอุตสาหกรรม ผู้วิจัยจึงสนใจกระบวนการใช้สาหร่ายดูดซับมวลสารออกจากแหล่งน้ำโดยจะศึกษาถึงความเข้มข้นของมวลสารในแหล่งน้ำด้วยกระบวนการดูดซับโดยใช้แบบจำลองทางคณิตศาสตร์ในการอธิบายปริมาณความเข้มข้นของมวลสารในแหล่งน้ำ

2 ทฤษฎีและหลักการ

2.1 กลไกของกระบวนการดูดซับ

การดูดซับ(Adsorption)เป็นกระบวนการกักพวกสารละลายหรือสารแขวนลอยขนาดเล็กซึ่งละลายอยู่ในน้ำให้อยู่บนผิวของสารอีกชนิดหนึ่ง โดยที่สารละลายหรือสารแขวนลอยขนาดเล็กนี้เรียกว่า สารถูกดูดซับ (Adsorbate) ส่วนของแข็งที่มีผิวเป็นที่เกาะจับของสารที่ถูกดูดติดเรียกว่า ตัวดูดซับ (Adsorbent) การดูดซับนี้จะเป็นการดูดติดแบบระหว่างสถานะ (Phase) ต่างๆ ทั้งสามสถานะ คือ ของเหลว (Liquid) ก๊าซ (Gas) และของแข็ง (Solid) ซึ่งมีได้ทั้งแบบ ของเหลว- ของเหลว ก๊าซ-ของเหลว ก๊าซ-ของแข็ง และ ของเหลว-ของแข็ง โดยในที่นี้จะพิจารณาถึงเฉพาะแบบ ของเหลว-ของแข็ง (Liquid –Solid Interface) ในการดูดซับโมเลกุลของสารละลายหรือสารแขวนลอยก็จะถูกกำจัดออกจากน้ำและไปเกาะติดอยู่บนตัวดูดซับ โมเลกุลของสารส่วนใหญ่จะเกาะจับอยู่กับผิวภายในโพรงของตัวดูดซับและมีเพียงส่วนน้อยเท่านั้นที่เกาะอยู่ที่ผิวภายนอก การถ่ายเทโมเลกุลจากน้ำไปหาตัวดูดซับเกิดขึ้นได้จนถึงสมดุลจึงหยุด ณ จุดสมดุล ความเข้มข้นของโมเลกุลในน้ำจะเหลือน้อยเพราะโมเลกุลส่วนใหญ่เคลื่อนที่ไปเกาะจับอยู่กับตัวดูดซับโดยในการเกาะติดจะมีแรงผลักดัน (Driving Force) อยู่ 2 แบบ คือ การดูดซับทางกายภาพ และการดูดซับทางเคมี[1]. ดังนั้นในกระบวนการดูดซับจะต้องมีการศึกษาก่อนว่าตัวดูดซับชนิดใดที่สามารถดูดซับมลสารนั้นได้อย่างเช่น มลสาร สีย้อม หรือมลสารชนิดอื่นๆเพราะเนื่องจากว่าการดูดซับจะดูดซับได้มากหรือน้อยจะขึ้นอยู่กับชนิดของตัวดูดซับด้วยและปัจจัยหลักของการดูดซับจะขึ้นอยู่กับ อุณหภูมิ ค่า pH และความดัน เป็นต้น และการพิสูจน์ว่าตัวดูดซับชนิดใดสามารถดูดซับมลสารได้มากนั้นโดยปกติของการทดลองเมื่อทำการทดลองแล้วจะนำผลของการทดลองมาทดสอบกับไอโซเทอมต่างๆเช่น แลงเมียร์ และฟรุนดิช เป็นต้นเนื่องจากว่าไอโซเทอมจะเป็นสิ่งที่บ่งบอกถึงลักษณะการดูดซับว่าเป็นลักษณะการดูดซับชั้นเดียวหรือหลายชั้นและมีแบบจำลองทางจลนพลศาสตร์ในการอธิบายถึงอัตราเร็วของการดูดซับซึ่งจะอธิบายรายละเอียดในหัวข้อถัดไป

2.2 แบบจำลองจลนพลศาสตร์ Pseudo – first order

การศึกษาอัตราเร็วปฏิกิริยาของการดูดซับตัวมลสารจะแสดงสมการดังนี้

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

โดยมีเงื่อนไข $q_t = 0$ ที่ $t = 0$ และ $q_t = q_t$ ที่ $t = t$ ซึ่งได้ผลเฉลยของสมการที่ (1) คือ

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

โดยที่ q_e เป็นความสามารถในการดูดซับมลสารที่สภาวะสมดุล(mg/g), q_t เป็นความสามารถในการดูดซับมลสารที่เวลา $t\ (mg/g)$, k_1 เป็นค่าคงที่อัตราเร็วของปฏิกิริยาอันดับที่หนึ่ง$(1/min)$ และ

t เป็นเวลาที่ใช้ในการดูดซับ(นาที) เมื่อทำการเขียนกราฟของ $\ln(q_e - q_t)$ กับ t จะได้กราฟเส้นตรง ดังนั้นค่าคงที่อัตราเร็วของ Pseudo – first order (k) หาได้จากความชันของเส้นตรง [3-5]. ในกระบวนการดูดซับของสาหร่ายจะสามารถอธิบายได้โดยใช้แบบจำลอง(1) ซึ่งได้มาจากการศึกษาการดูดซับมวลสารบนผิวของสาหร่าย.

3 แบบจำลองทางคณิตศาสตร์

3.1 สมการการดูดซับ

ในงานวิจัยนี้จะสนใจความเข้มข้นของมวลสารที่เหลืออยู่ในแหล่งน้ำที่เกิดจากการเอาความเข้มข้นของมวลสารทั้งหมดลบออกจากความเข้มข้นที่สาหร่ายดูดซับมวลสาร เพราะฉะนั้นแล้วรูปแบบสมการจะอยู่ในรูปกฎอนุรักษ์มวล ดังนั้นจึงใช้รูปแบบสมการ Pseudo first order ในการแปลงรูปมวลของมวลสารที่ถูกสาหร่ายดูดซับดังนี้

ปริมาณมวลสารในน้ำ = ปริมาณมวลสารทั้งหมด – ปริมาณมวลสารในสาหร่าย

จากสมการ (1) เมื่อทำการหาผลเฉลยจะอยู่ในรูป

$$q_t = q_e + e^{-k_1 t}(q_0 - q_e) \qquad (3)$$

จาก

$$q_t = \frac{m}{m_g} = \frac{\text{ปริมาณมวลสารที่อยู่บนสาหร่าย(mg)}}{\text{มวลสาหร่าย(g)}}$$

$$q_e = \frac{m_e}{m_g} = \frac{\text{ปริมาณมวลสารที่อยู่บนสาหร่ายในสภาวะสมดุล(mg)}}{\text{มวลสาหร่าย(g)}}$$

$$q_0 = \frac{m_0}{m_g} = \frac{\text{ปริมาณมวลสารที่อยู่บนสาหร่ายในสภาวะเริ่มต้น(mg)}}{\text{มวลสาหร่าย(g)}}$$

โดยที่ q_t, q_e, q_0 เป็นความสามารถในการดูดซับมวลสาร(mg/g) ความสามารถในการดูดซับมวลสารที่สภาวะสมดุล(mg/g) และความสามารถในการดูดซับมวลสารเริ่มต้น (mg/g) ตามลำดับ จากสมการ (3) นำ m_g คูณตลอดทั้งสมการจะได้

$$m = m_e + e^{-k_1 t}(m_0 - m_e) \qquad (4)$$

และจากสูตรความเข้มข้น(C) $= \frac{\text{มวล}}{\text{ปริมาตร}} = \frac{M}{V}$

ปริมาณมวลสารในน้ำ = ปริมาณมวลสารทั้งหมด – ปริมาณมวลสารในสาหร่าย

$$M = M_0 - \left(m_e + e^{-k_1 t}(m_0 - m_e)\right)$$

จากสมการที่อยู่ในรูปมวล (mg) จะเปลี่ยนให้อยู่ในรูปความเข้มข้น (mg/L) จะได้ว่า

$$C = (C_0 - C_{al}) + e^{k_1 t} C_{al} \qquad (5)$$

ที่เวลา (t) จะได้

$$\frac{dC}{dt} = -k_1 C_{al} e^{-k_1 t} \qquad (6)$$

จากสมการที่ (5) จัดรูปสมการที่ (6) ให้อยู่ในรูปแบบ Autonomous system จะได้ว่า

$$\frac{dC}{dt} = -k_1 \left(C - (C_0 - C_{al})\right) \qquad (7)$$

โดยที่ C เป็นความเข้มข้นของมวลสารที่เหลืออยู่ในแหล่งน้ำ (mg/L) C_0 เป็นความเข้มข้นของมวลสารทั้งหมด (mg/L) C_{al} เป็นความเข้มข้นที่สาหร่ายดูดซับมวลสารได้มากที่สุด (mg/L) k_1 เป็นอัตราเร็วในการเกิดปฏิกิริยา (1/min) t เป็นเวลา (min)

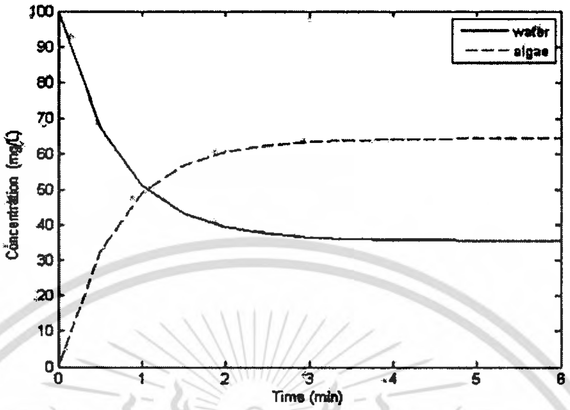
จากงานวิจัยการกำจัดสีย้อมจากโรงงานฟอกสีที่มีการดูดซับด้วยสาหร่าย Pithophora sp.ในแหล่งน้ำจืดโดยได้ทำการทดลองการดูดซับสีย้อมโดยการใช้มวลชีวภาพสาหร่าย Pithophora sp.เป็นตัวดูดซับโดยตัวแปรที่ศึกษาจะเป็นความเข้มข้นเริ่มต้นของสีย้อม ความเข้มข้นของสาหร่าย และค่า pH ของสารละลายและจะทำการดูดซับด้วยสาหร่าย Pithophora sp. ที่อุณหภูมิ 300 องศาเซลเซียสเป็นเวลา 50 นาทีซึ่งปริมาณความเข้มข้นของสีย้อมที่ศึกษาอยู่ในช่วง 20 – 100 mg/L ซึ่งการดูดซับของสาหร่าย Pithophora sp. ที่อุณหภูมิ 300 องศาเซลเซียสปริมาณของการดูดซับที่มากสุดมีค่าเป็น 117.647 mg/g เป็นที่แน่ชัดแล้วว่าสาหร่ายสามารถดูดซับได้ภายใต้เงื่อนไขเหล่านี้ซึ่งแสดงให้เห็นได้ว่าสามารถนำมาเป็นตัวดูดซับทางชีวภาพได้โดยที่จากการทดลองสาหร่ายสามารถดูดซับสีย้อมได้ที่ความเข้มข้น 64.4 mg/L ที่ความเข้มข้นมากสุดของสีย้อม 100 mg/L และได้ทำการแสดงข้อมูลดัง Table 1. [2]

Table 1
Kinetic constants for methylene blue onto thermally activated *Pithophora* sp.

C_0 (mg/L)	1 order constants		Reversible first order kinetics					Pseudo-second order kinetics			
	K_1	R_1^2	K_1	K_2	K	K'	R_1^2	K_{II}	h	q_e	R_{II}^2
20	1.349458	0.9973	1.72	0.1156	14.87	1.835	0.8607	8.13E−03	384.2109	217.39	0.9908
40	2.134287	0.9587	1.64	0.2342	7	1.8694	0.9378	4.46E−03	713.6	400	0.9893
60	1.75028	0.9293	1.27	0.2239	5.67	1.4994	0.8999	1.50E−03	666.2289	666.67	0.9646
80	1.864279	0.9015	1.3	0.325	4	1.6253	0.8799	1.88E−03	1111.11	769.23	0.9849
100	1.417727	0.9396	1.01	0.2845	3.53	1.2922	0.9285	1.34E−03	1110.742	909.09	0.9881

K_1 (min^{-1}), K_{II} (g/mg h), h (mg/g h), q_e (mg/g), K_1 (h^{-1}), K_2 (h^{-1}).

จากสมการ(7) เมื่อนำมาวาดกราฟความเข้มข้นของสีย้อมที่เหลือในแหล่งน้ำเทียบกับเวลาและความเข้มข้นของสีย้อมที่อยู่บนสาหร่าย Pithophora sp. เทียบกับเวลา โดยใช้ข้อมูลของการทดลองความเข้มข้นสีย้อม(C_0) 100 mg/L ความเข้มข้นที่สาหร่าย Pithophora sp. ดูดซับสีย้อมมากสุด(C_{al}) 64.4 mg/L และค่าคงที่ของอัตราเร็วการเกิดปฏิกิริยาอันดับที่หนึ่ง (k_1) 1.42 (1/min) ซึ่งแสดงดังรูปที่ 1.



รูปที่ 1. แสดงความเข้มข้นของสีย้อมในแหล่งน้ำ (C) เทียบกับเวลา (t) และความเข้มข้นที่สาหร่าย Pithophora sp. ดูดซับสีย้อมมากสุด (C_{al}) เทียบกับเวลา (t)

จากกราฟจะเห็นได้ว่าความเข้มข้นสีย้อมที่สาหร่าย Pithophora sp. ดูดซับได้มากสุดเท่ากับ 64.39 mg/L และความเข้มข้นสีย้อมที่เหลืออยู่ในแหล่งน้ำเท่ากับ 35.61 mg/L ซึ่งเมื่อนำความเข้มข้นทั้งสองมารวมกันจะมีค่าเท่ากับความเข้มข้นเริ่มต้น (C_0) ที่ 100 mg/L

4 สรุปผล

จากกราฟความเข้มข้นของสีย้อมที่เหลือในแหล่งน้ำเทียบกับเวลาและความเข้มข้นของสีย้อมที่อยู่บนสาหร่าย Pithophora sp.เทียบกับเวลาโดยใช้ข้อมูลของการทดลองที่ความเข้มข้นสีย้อม (C_0) เท่ากับ 100 mg/L ความเข้มข้นที่สาหร่าย Pithophora sp. ดูดซับมากสุด (C_{s1}) มีค่าเป็น 64.4 mg/L และค่าคงที่ของอัตราเร็วการเกิดปฏิกิริยาอันดับที่หนึ่ง (k_1) คือ 1.42 (1/min) ทำให้เห็นได้ว่าผลของกราฟมีความสอดคล้องกับผลของการทดลองทำให้เห็นได้ว่าสมการของแบบจำลองมีความเหมาะสมกับการดูดซับ และจากกราฟที่จุดตัดของความเข้มข้นสีย้อมที่เหลือในแหล่งน้ำกับความเข้มข้นของสีย้อมที่มากสุดที่อยู่บนสาหร่าย Pithophora sp.แสดงให้เห็นได้ว่าจะมีค่าเท่ากับครึ่งหนึ่งของความเข้มข้นเริ่มต้น ($C_0/2$)

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Modeling for Metals Contaminated Wastewater by Algae Adsorption *

P. Chankitkan[1], B. Pimpunchat[1], K. Chamsri[1], W. Triampo[2],
S. Amornsamankul[3]

[1]Industrial Mathematics Research Unit and Department of Mathematics, King Mongkut's
Institute of Technology Ladkrabang, Bangkok 10520, Thailand;
Center of Excellence in Mathematics, Bangkok 10400, Thailand.
chankitkan_p@hotmail.com; knbusaya@kmitl.ac.th; kckannan@kmitl.ac.th
[2]Department of Physics, Mahidol University, Bangkok 10400, Thailand;
Institute for Innovative Learning, Mahidol University, Nakorn Prathom 73170, Thailand ;
Center of Excellence in Mathematics, Bangkok 10400,Thailand.
scwtr@mahidol.ac.th, Wtriampo@gmail.com
[3]Department of Mathematics, Mahidol University, Bangkok 10400, Thailand;
Center of Excellence in Mathematics, Bangkok 10400, Thailand.
somkid.amo@mahidol.ac.th

Abstract

We studied the ability of adsorption of algae in wastewater polluted by alloys. A mathematical model is developed to describe the biosorption of metals by algae in the contaminated water. The analytic solution is obtained by using Similarity method. The result provides understanding the advection and diffusion of the metals in the contaminated water at various times and positions. It was found that the concentration of metals in the contaminated water consisting of the algae decreases over time and asymptotically reaches the equilibrium state. Moreover, the analytic results were validated by comparing with experimental data. This work is expected to greatly benefit an environmental science particularly concerning the wastewater treatment.

Keywords: Biosorption, Wastewater, Advection, Diffusion, Similarity method, Equilibrium state.

1 Introduction

Nowadays wastewater is one of the most problems of environment stem from community, agriculture and industrial effluents which are different amount of the byproduct of industrialization.With the industrial increase nowadays the problem of wastewater has become even more severe especially when lacking of good wastewater management. Industrial wastewaters differ in their impurities and here metals contaminated wastewater is considered for treatment aspect using microalgae. Normally, wastewater treatment can be as simple as chemical addition or as complex as the combination of multiple unit processes for a complete water treatment system. Here the process of adsorption is focused. The microalgae is used as an adsorption agent, thus the process is so called biosorption. Because aerobic treatment reservoir in our system has abundant the algae and the aquatic plant, they then act as wastewater cleaning metal alloys agent in the contaminated water. The mathematical model is developed to describe the biosorption of metals by algae in the contaminated water and the analytic solution is obtained for having insight into the problem.[1-3]

In (2005)[4] Kumar and co-workers studied about adsorption of malachite green onto *Phithophora sp.* with the initial malachite green of (20-100 mg/l). They found that algae posses some capacity to uptake 64.4 mg/g at higher dye concentration of 100 mg/l and approach the equilibrium state around at 50 minutes. Recently,[5] Sukhuum and Inthorn

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*Corresponding author B.Pimpunchat: knbusaya@kmitl.ac.th.

have studied about removal of Cr^{+3} by *Rivularia sp.* and *Stigonema minutum*. They considered the initial concentration of Cr^{+3} 500 mg/l and found that Rivularia sp. and Stigonema minutum had the highest Cr^{+3} adsorption at 38.27 and 43.59 mg/g then reach equilibrium state at 120 minutes.

In this study the ability of adsorption of algae in wastewater polluted by alloys was investigated and mathematically analyzed particularly on concentration of metals in contaminated water by using mathematical model at any time and various distance.

2 Model formalism

By using the conservation of mass, the amount of metals remaining in after the contaminated water is given by the initial amount of the alloy in the wastewater minus and the amount adsorbed on the algae.

$$C = C_0 - C_t \tag{1}$$

where C is the concentration of metals in the remaining in the contaminated water (mg/l), C_0 is the initial concentration of metals in the contaminated water (mg/l), and C_t is the concentration adsorbed on the algae at any time(mg/l). The remaining concentration of metals in the contaminated water is obtained from the following mass balance

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} + f(t) \tag{2}$$

where D_x is a diffusion coefficient; v is the velocity in the x direction , t is time of adsorption. To find the function $f(t)$, we begin with by pseudo first order model.

$$\frac{dq}{dt} = k_1(q_{al} - q) \tag{3}$$

where q_{al} and q are the amount of adsorbed metals on algae at equilibrium and at any time (mg/g), respectively , k_1 is the rate constant first order biosorption.

Integrating Equation (3);

$$\int_0^{q_t} \frac{dq}{q_{al} - q} = \int_0^t k_1 \, dt$$

$$q_t = q_{al} + e^{-k_1 t}(q_0 - q_{al}) \tag{4}$$

Then formula ability adsorp of algae

$$q_0 = \frac{M_0}{M_s}, \; q_t = \frac{M_t}{M_s}, \; q_{al} = \frac{M_{al}}{M_s} \tag{5}$$

where q_t is the amounts of adsorbed metals on algae at any time (mg/g), M_s is the mass of algae (g), M_0, M_t and M_{al} is the mass of adsorbed metals on algae at initial time, any time and equilibrium state(mg), respectively.

Solving (4) and (5), we obtain;

$$M_t = M_{al} + e^{-k_1 t}(M_0 - M_{al}) \tag{6}$$

Let M is the remaining mass of metals in the contaminated water (mg). From conservation of mass we have:

$$M = M_{total} - M_t \tag{7}$$

where M_{total} is total mass of metal (mg).

Substituting (6) into conservation of mass (7), we obtain;

$$M = M_{total} - (M_{al} + e^{-k_1 t}(M_0 - M_{al})) \tag{8}$$

Let V be a constant volume (l). Dividing Equation (8) by V, we have:

$$C = e^{-k_1 t} C_{al} + (C_0 - C_{al}) \tag{9}$$

Differentiating (9) with respect to t, equation (9) can be rewritten as:

$$f(t) = -k_1(C - (C_0 - C_{al})) \tag{10}$$

Substituting (10) into (2) yields:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - k_1(C - (C_0 - C_{al}))$$

Let $C^* = C - C_0 + C_{al}$:

$$\frac{\partial C^*}{\partial t} = D_x \frac{\partial^2 C^*}{\partial x^2} - v\frac{\partial C^*}{\partial x} - k_1 C^* \tag{11}$$

The initial condition is

$$C^*(x,0) = C_0 \tag{12}$$

and the boundary conditions are

$$C^*(0,t) = C_1,\ \frac{\partial C^*}{\partial x}(L,t) = 0,\ 0 \le x \le L \tag{13}$$

where C_1 is a constant. The equation (11) is the mathematical model for this problem. We derive the similarity solution of equation (11) using the group theory method of similarity analysis.

3 Similarity Analysis by Invariance Groups

3.1 The Analysis of invariance

There are several thechniques for solving partial differential equation by using similarity methods such as Free Parameter Method, Separation of Variables Method, Group Theory Method and Dimensional Analysis Method. Among these methods, we consider to apply the group theory method of similarity methods for solving the equation (11).

To solve Equation (11) using the one parameter group of transformation

$$\begin{aligned} T &= a^n t \Rightarrow t = a^{-n}T \\ X &= a^m x \Rightarrow x = a^{-m}X \\ C &= a^p C^* \Rightarrow C^* = a^{-p}C \end{aligned} \tag{14}$$

where T, X, and C are functions of t, x, and C^*, respectively, 'a' is an variable and m,n, p are the parameters.

Employing Equation (14) into Equation (11), we have:

$$\frac{\partial C^*}{\partial t} - D_x \frac{\partial^2 C^*}{\partial X^2} + v\frac{\partial C^*}{\partial X} + k_1 C^* = a^{-p+n}\frac{\partial C}{\partial T} - D_x a^{-p+2m}\frac{\partial^2 C}{\partial X^2} + v a^{-p+m}\frac{\partial C}{\partial X} + k_1 a^{-p} C \tag{15}$$

Equating the powers of 'a', becomes;

$$-p+n = -p+2m = -p+m = -p$$

Let

$$\begin{aligned} -p+2m &= -p+m \Rightarrow m = 0 \\ -p+n &= -p+m \Rightarrow m = 0,\ n = 0 \end{aligned}$$

Employing these values in Equation (15) , becomes ;

$$\frac{\partial C^*}{\partial t} - D_x \frac{\partial^2 C^*}{\partial X^2} + v\frac{\partial C^*}{\partial X} + k_1 C^* = a^{-p}\left(\frac{\partial C}{\partial T} - D_x \frac{\partial^2 C}{\partial X^2} + v\frac{\partial C}{\partial X} + k_1 C\right)$$

If $p \equiv 0$then the equation will reduce into the constant conformally invariant.

3.2 Similarity Solution

Let

$$\eta = xt^{s} \tag{16}$$

To reduce equation (21) to the constant conformaly invariant;

$$\eta = xt^{s} = \left(a^{-m}X\right)\left(a^{-n}T\right)^{s} = a^{-m-ns} \cdot XT^{s} \quad \left(only\ if - m - ns = 0,\ s = \frac{-m}{n}\right)$$

Hence

$$\eta = xt^{\left(-\frac{m}{n}\right)}$$

Again consider the another function g which is the function of also the dependent variable C^* as well as the independent variable t

Let

$$g = C^* t^{r} \tag{17}$$

To reduce into constant conformaly invariant;

$$g = \left(a^{-p}C\right)\left(a^{-n}T\right)^{r} = a^{-p-nr}CT^{r} \quad \left(only\ if - p - nr = 0,\ r = \frac{-p}{n}\right)$$

Then

$$g = C^* t^{\left(-\frac{p}{n}\right)}$$

Choose: $g = C^* t^{\left(-\frac{p}{n}\right)} = F(\eta)$

Now, we have to define the value of $F(\eta)$:

$$\begin{aligned} \frac{\partial C^*}{\partial t} &= t^{\left(\frac{p-n}{n}\right)}\left(\frac{pF(\eta) - m\eta F'(\eta)}{n}\right) \\ \frac{\partial C^*}{\partial x} &= t^{\left(\frac{p-m}{n}\right)}F'(\eta) \\ \frac{\partial^2 C^*}{\partial x^2} &= t^{\left(\frac{p-2m}{n}\right)}F''(\eta) \end{aligned} \tag{18}$$

Substituting (18) into (11) , can be written:

$$t^{\left(\frac{p-n}{n}\right)}\left(\frac{pF - m\eta F'}{n}\right) - D_x t^{\frac{p-2m}{n}}F'' + vt^{\frac{p-m}{n}}F' + k_1 t^{\frac{p}{n}}F \tag{19}$$

From: $-p + n = -p + 2m = -p + m = -p$

Thus: $-\left(\frac{p-n}{n}\right) = -\left(\frac{p-2m}{n}\right) = -\left(\frac{p-m}{n}\right) = -\frac{p}{n}$

We consider:

1). if $\frac{p-n}{n} = 0 \Rightarrow \frac{p}{n} = 1$ & $\frac{p-2m}{n} = 0$ then $\frac{p}{n} = \frac{2m}{n} \Rightarrow \frac{m}{n} = \frac{1}{2}$

2). if $\frac{p-n}{n} = 0 \Rightarrow \frac{p}{n} = 1$ & $\frac{p-m}{n} = 0$ the $\frac{p}{n} = \frac{m}{n} \Rightarrow \frac{m}{n} = 1$

We choose case 2). then equation (19) becomes:

$$D_x F''(\eta) + (\eta - v)F'(\eta) + (1 + k_1)F(\eta) = 0 \tag{20}$$

The initial condition is

$$F(\eta(x,0)) = 0 \tag{21}$$

and the boundary conditions are

$$F(\eta(0,t)) = (C_1 - C_0 + C_{al})\,t^{\left(-\frac{p}{n}\right)} \quad , t \geq 0 \quad , \frac{\partial F(\eta(L,t))}{\partial \eta} = 0 \quad , \forall_{x,t} \tag{22}$$

From equation (20) assuming that: $F^{(\eta)} = e^{a\eta}$

We get: $e^{a\eta}\left(D_x a^2 + (\eta - v)a - (1 + k_1)\right) = 0 \quad , e^{a\eta} \neq 0$

General solution is form: $F(\eta) = c_1 F_1(\eta) + c_2 F_2(\eta)$
Thus;

$$F(\eta) = c_1 e^{\left(-\frac{(\eta-v)}{2D_x} + \frac{1}{2}\sqrt{\left(\frac{\eta-v}{D_x}\right)^2 + \frac{4(1+k_1)}{D_x}}\right)\eta} + c_2 e^{\left(-\frac{(\eta-v)}{2D_x} - \frac{1}{2}\sqrt{\left(\frac{\eta-v}{D_x}\right)^2 + \frac{4(1+k_1)}{D_x}}\right)\eta}$$

Substituting the boundary conditions to find the arbitrary constants, we have;

$$F(\eta) = (C_1 - C_0 + C_{al})\, t^{\left(-\frac{m}{n}\right)} e^{\left(-\frac{(\eta-v)}{2D_x} - \frac{1}{2}\sqrt{\left(\frac{\eta-v}{D_x}\right)^2 + \frac{4(1+k_1)}{D_x}}\right)\eta}$$

or

$$C(x,t) = (C_1 - C_0 + C_{al})\, e^{\left(-\frac{\left(xt^{\left(-\frac{m}{n}\right)} - v\right)}{2D_x} - \frac{1}{2}\sqrt{\left(\frac{xt^{\left(-\frac{m}{n}\right)} - v}{D_x}\right)^2 + \frac{4(1+k_1)}{D_x}}\right) xt^{\left(-\frac{m}{n}\right)}} \tag{23}$$

4 Results and Discussion

In this research, We use experimental data of the adsorption of malachite green onto *Phithophora sp.*[4]. We shows the comparing analytical results with experimental data also with the average analytical result.

In research [9] studied adsorption of chromium (VI) from electroplating factory by chitosan resin. We use experiment data for comparing analytical result and average analytical result as shown in Figure 1-4.

5 Conclusion

The proposed results of concentration of metals contaminated in water with algae showed that the concentrations of contaminated water in mathematical model decrease to equilibrium state in every case. The results from two related papers, chromium adsorption with chitosan resin and dye adsorption by Phithophora sp. had been compared with our results. There has been satisfactory agreement between the theoretical mathematical model and experimental data.

6 Acknowledgments

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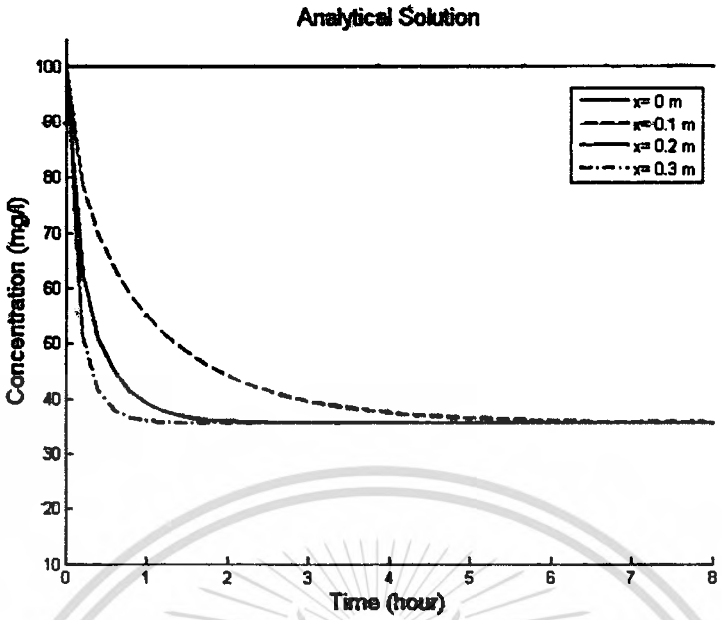


Figure 1: Shows the remainder of concentration of dye in water with analytic solution after adsorption by *Phithophora sp*. The result shows any position decrease and asymptotically reaches the equilibrium state at 35.7 mg/l

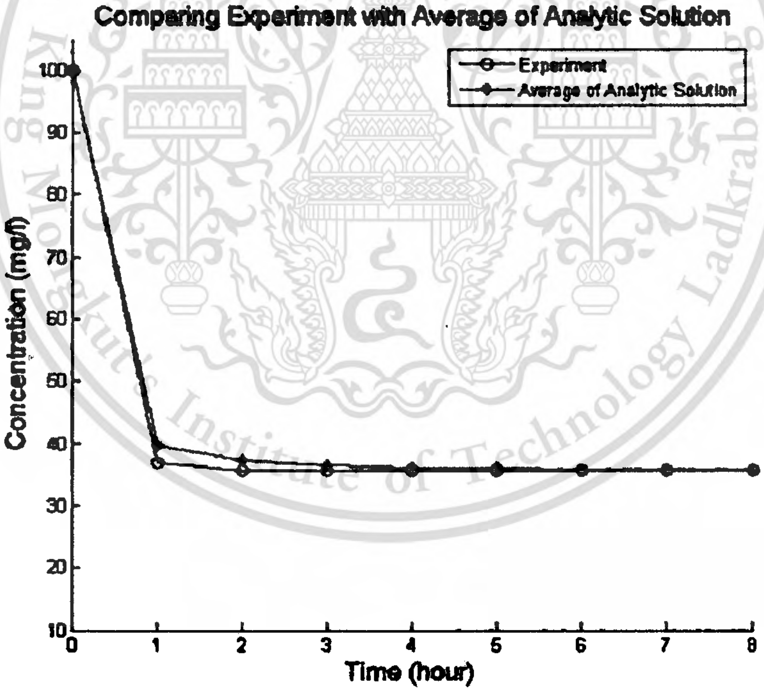


Figure 2: Comparing experiment with average analytic solution found that experimental result conform to average analytic solution and asymptotically reaches the equilibrium state 35.7 mg/l at 50 minutes.

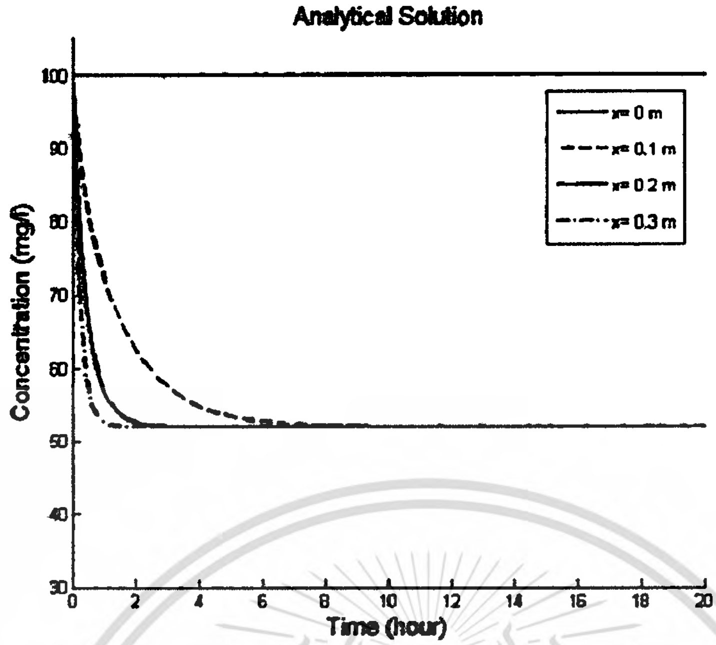


Figure 3: Shows the remainder of concentration of chromium (VI) in water with analytic solution after adsorption by chitosan resin. The result shows any position decrease and asymptotically reaches the equilibrium state at 52.2 mg/l

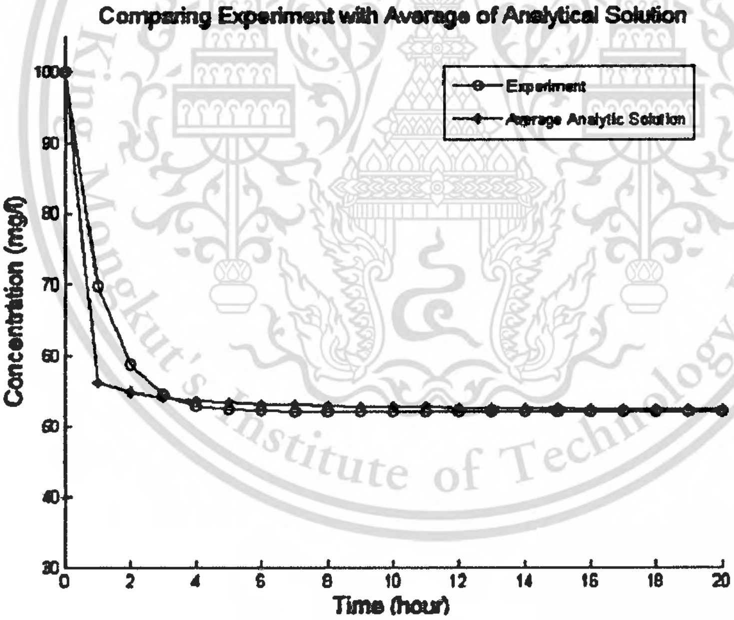


Figure 4: Comparing experiment with average analytic solution found that experimental result conform to average analytic solution and asymptotically reaches the equilibrium state 52.2 mg/l at 6 hour.

APPENDIX B.

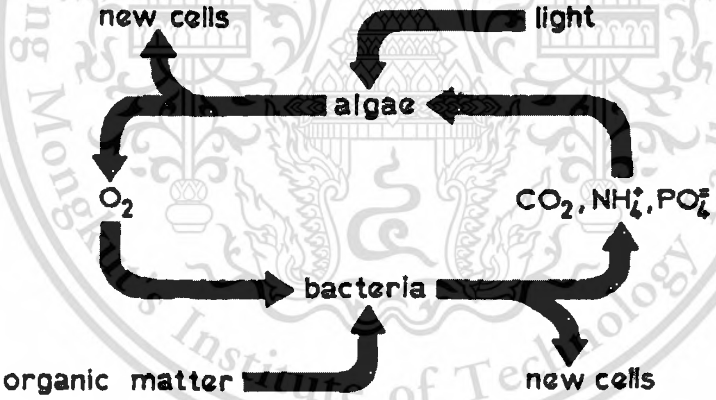
WASTEWATER TREATMENT PONDS

Wastewater Treatment Ponds [1]

There are mainly three types of pond used in wastewater treatment; anaerobic, facultative and maturation ponds. The typical outline of treatment ponds is first a deep anaerobic pond where particles settle followed by one or more shallow aerobic ponds. In general there is a high reduction of nitrogen but phosphorus removal is quite low.

Aerobic ponds – facultative and maturation ponds

The treated water on the top of the anaerobic pond is lead further to a shallow aerobic pond where other biological activities take over. Due to the supply of oxygen, dengradation of nutrients and harmful substance are mainly done by heterotrophic bacteria and algae. These types require larger areas. Facultative ponds remove BOD as well as reduce pathogens. The treatment is based on the algal and bacterial mutualism which occurs in the upper layer where the sunlight can penetrate. The algae produce oxygen through photosynthesis, which is used by the bacteria. The bacteria release ammonia, carbon dioxide and phosphate which in turn are used by the algae. Because of the photosynthetic activity of the algae, oxygen and pH varies in the pond over day and night.



Algal – bacterial mutualism in facultative and maturation pond

Maturation ponds would be placed last in the sequence. They are aerobic through the whole depth and functions as a pathogen reducer. This is due is to a high pH as well as the high concentration of dissolved oxygen as a result of algae activity. Apart from efficiently removing fecal coliforms and viruses, it reduce parasites up to 100%.

Facultative ponds

Facultative ponds usually have a depth of 1.5 – 2 meter and retention period of 20 – 50 days. It could be designed by estimating the volume, surface area and retention time. As the mean temperature is surveyed before, the biological breakdown rate and BOD removal can be found out, which the retention time is calculate from. The depth of the pond is determined by the climate of this area. For tropical climate the depth could be 1 meter, in temperate climate 50 cm could be added and in cold area a additional 1 meter.

Anaerobic ponds

The design of anaerobic ponds is according to the temperature, pH and the putflow quality demanded. Anaerobic ponds normally have a depth between 2 – 5 m and receive high BOD loads (more than 100g BOD/m^3.day). The pH of the waste water has to be ensured more than 6.2 before entering the anaerobic process and a short retention time (2 – 4 day) is usually chosen.

Aerobic ponds

The design of the aerobic ponds should follow three principles. Firstly, give the minimum depth to the pond while making the maximum algae production. Secondly, equalize the BOD removal and the pathogen control. At last, encourage mixing and aeration to support the activity of aerobic bacteria.

Maturation ponds

The principle factor of the design of the maturation ponds is the detention time. This and the number of the ponds are determined by the degree of bacterial purification of the ponds. Commonly, the depth of the ponds is 1.5 – 2 m and the detention time is 5 – 15 days. It is essential to arrange the maturation ponds in series with the preceding ponds to obtain the efficient reduction of the faecal bacteria

APPENDIX C.

ADSORPTION

Isotherm adsorption [2]

Adsorption is usually described through isotherms, that is, function which connect the amount of amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, etc.

Langmuir isotherm

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2. Adsorbed molecules do not interact.
3. All adsorption occur through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

BIOGRAPHY

NAME	Ms. Pornwilai Chankitkan
DATE OF BIRTH	December 6, 1986
PLACE OF BIRTH	Uthaithani, Thailand
ATTENDED INSTITUTION	King Mongkut's Institute of Technology Ladkrabang,2005-2008 Bachelor of Science Applied Mathematics King Mongkut's Institute of Technology Ladkrabang, 2009-2012 Master's Degree Applied Mathematics
HOME ADDRESS	12 Moo 11, Thambom Nong Klang Dong, Amphur Thapthan, Uthaithani, 61120, Thailand
E-MAIL	chankitkan_p@hotmail.com